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RESEARCH AND EDUCATION

Effect of hydrothermal aging on the microhardness of high- and low-viscosity conventional and additively manufactured polymers

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ABSTRACT

Statement of problem. Studies on the microhardness of novel additively manufactured polymers compared with well-established low- and high-viscosity composite resins with regard to chemical composition are lacking.

Purpose. The purpose of this in vitro study was to evaluate the effect of hydrothermal aging on the microhardness of various conventional and additively manufactured polymers.

Material and methods. Cylindrically shaped specimens (N=240, n=10 per group) (Ø10×2 mm) were either additively manufactured (6 groups) or conventionally (6 groups) manufactured by using 3D (Optiprint Temp [OP; Dentona]; C&B MFH [ND; NextDent]; Saremco print CROWNTEC [SA; Saremco Dental AG]; Temp Print [TP; GC]; 3DELTA ETEMP [DM; Deltamed]; MED690 [ST; Stratasys, Ltd]) or conventional low (Gradia Direct [GR; GC]; Clearfil Majesty [CM; Kuraray Noritake]; Tetric EvoCeram [TE; Ivoclar Vivadent AG]) and high (Gradia Direct Flo [GR-F; GC]; Clearfil Majesty Flow [CM-F; Kuraray Noritake]; Tetric EvoFlow [TE-F; Ivoclar Vivadent AG]) viscous materials. All specimens were randomly allotted to 2 different aging methods (no-aging [dry] or aging by thermocycling [TC], ×6000, 5 °C-55 °C) and Vickers hardness (VH) tested (ZHV30; Zwick). Three indentations were made on each specimen (0.98-N load, duration 15 seconds). The calculated average microhardness value of each specimen was statistically analyzed by using 2-way ANOVA and Tukey post hoc tests (α=.05). Two-parameter Weibull distribution was calculated to predict the reliability of material type and aging method on VH.

Results. The mean ±standard deviation VH ranged between 17 ±0.5 VHN and 68 ±0.5 VHN in the following ascending order: group ST[a]<OP[b], ND[b]<SA[c], TP[c]<GR[d], GR-F[d]<DM[e], TE-F[e]<CM[f]<TE[g]<CM-F[h]. The groups with the same superscript were not significantly different from each other (P>.05). The mean ±standard deviation of HV for aged (37 ±1 VHN) and nonaged (35 ±1 VHN) specimens were statistically similar (P>.05). The Weibull distribution values presented the highest shape for the aged group SA (37.81).

Conclusions. The choice of the material had a significant effect and resulted in lower hardness for the 3-dimensionally printed materials than for the conventional composite resins. Under fatigue conditions, the choice of the material showed no significant difference when the Vickers microhardness was evaluated. (J Prosthet Dent 2022;■:■-■)

Conflict of Interest: The authors acknowledge the companies Deltamed, GC, Ivoclar AG, Kuraray Noritake, Nextdent, Saremco Dental AG, and Stratasys Ltd for generously providing the materials tested in this study.

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Clinical Implications

The integration of urethane dimethacrylates alone into additively manufactured polymers does not ensure high microhardness. The addition of triethylene glycol dimethacrylate (TEGDMA) to the conventional groups or a mixture of bisphenol A-glycidyl methacrylate (bis-GMA) and urethane dimethacrylates appears to provide favorable Vickers hardness.

Restoring lost dental hard tissues can be achieved by using direct chairside or indirect laboratory manufacturing techniques.[1] In recent years, dental polymers have been a commonly used material group.[2] The composition, filler content, shape and size, interlocking between filler particles, and interfacial interaction between the filler particles and the matrix resin affect the viscosity and polymerization kinetics of composite resins. Viscosity, however, influences the mechanical properties and the resistance to indentation of dental polymers.

The first dental polymers consisted of monomethacrylate (MMA) monomers and were replaced by dimethacrylates such as a bisphenylglycidyl dimethacrylate (bis-GMA) to overcome their high shrinkage and poor resistance to wear.[2] As moderate polymerization shrinkage occurred when bis-GMA was used, the filler content was increased, and bis-GMA was replaced by silorane monomers, resulting in less shrinkage and improved color stability compared with dimethacrylate polymers but inadequate mechanical properties.[3,4] To further improve the degree of polymerization and minimize the polymerization shrinkage, triethyleneglycol dimethacrylates (TEGDMA), urethane dimethacrylates (UDMA), and bisphenol A diglycidyl methacrylate ethoxylate (bis-EMA) were incorporated into the polymer matrix, resulting in lower water absorption and solubility as a consequence of the cross-linked network formation.[5] The addition of nanoparticles reduced polymerization shrinkage further but did not prevent shrinkage stress.[6] Stress at the adhesive interface remained a significant problem, especially in the intraoral environment, simulated in the present study by using hydrothermal aging conditions that could lead to nanoleakage or microleakage and failure of the restoration.[6]

Composite resins can be classified as macrofill, minifill, and microfill based on filler particle size or as hybrid composite resins. However, more recently, they have been classified as flowable, of medium viscosity, and packable based on viscosity or fluidity. Viscosity has been increased by a higher filler content, modified particle morphology, or the incorporation of glass fibers. Flowable restorative composite resins have a viscosity lower than 1 kPa·s, while the viscosity of highly filled composite resins is higher than 100 kPa·s.[7]

The introduction of novel digital technologies in dentistry, such as 3-dimensional (3D) printing, has led to the introduction of new polymers for biomedical application.[8] Different additive manufacturing processes and materials have been implemented in dentistry, and additive manufacturing allows the individualized and cost-effective processing of materials producing personalized end products.[9] Furthermore, additive technologies are expected to replace current subtractive methods as they enable material reuse and mass production.[10]

In restorative dentistry and prosthodontics, additively manufactured polymers have been widely used for the fabrication of dental casts, interim restorations, and occlusal devices.[11,12] As 3D-printed materials have poor mechanical properties, their application in prosthodontics is limited to short-term partial crowns and fixed and removable dental prostheses.[13,14]

The properties of the material and the surrounding environment in the oral cavity greatly affect the long-term performance of composite resin restorations. The properties include mechanical, physical, and biological parameters, for example, surface microhardness. Information provided by the manufacturers regarding the viscosity of additively manufactured polymers is sparse. The Brookfield viscosity of only 1 material in the present study (C&B MFH; NextDent) was found, reporting a range of 0.8 to 1.3 Pa·s, around 1000 times less than the viscosity of flowable restorative composite resins.[15]

Surface microhardness is a physical property influenced by the cohesive strength and wear behavior of the material corresponding to the resistance of the polymeric material to indentation and correlating with the durability of dental restorations.[16] Microhardness has also been used to evaluate the degree of conversion (DC) of polymeric materials. The higher the filler content and DC, the higher the surface hardness, with improved long-term outcomes.[17] However, to predict the outcome of additively manufactured polymers in restorative dentistry and to allow their use as long-term restorative materials, their mechanical properties need further investigation.[18-24]

The present study assessed the mechanical properties of additively manufactured polymers regarding their chemical composition by using microhardness tests and compared them with conventional low- and high-viscosity composite resins. The additively manufactured polymers tested in this study were marketed for interim

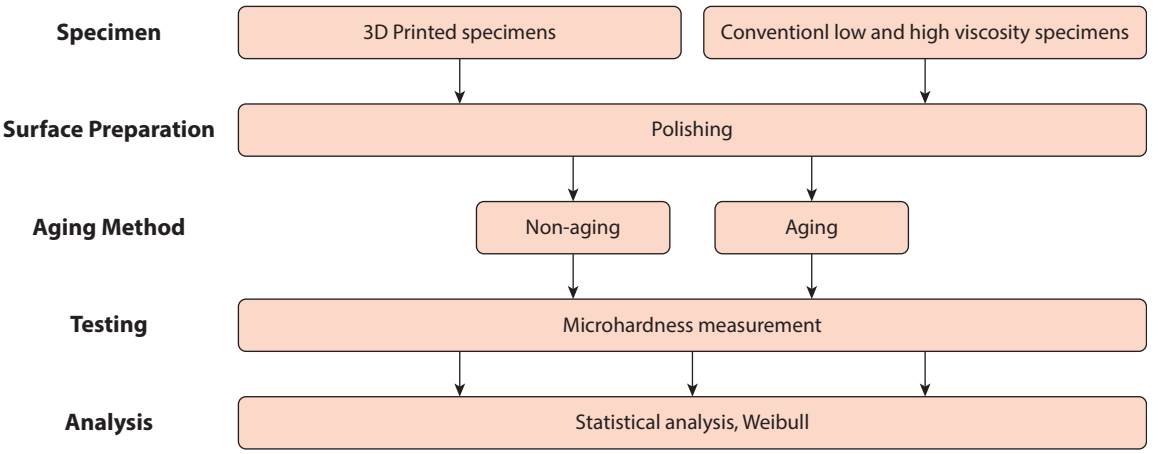

Figure 1. Experimental flowchart.

Table 1. Chemical compositions and manufacturers of restorative materials tested

Material	Chemical Composition	Manufacturer	Approval
Optiprint Temp (OP)	Bisphenol a-ethoxylate (2 eo/phenol) dimethacrylate, aliphatic difunctional methacrylate<50, 2,2′-ethylenedioxydiethyl dimethacrylate<40, aliphatic urethane acrylate<20, phosphine oxide<2.5%	Dentona	FDA-approved[a] Class IIa CE certified
C&B MFH (ND)	Methacrylic oligomers, methacrylate monomer, inorganic urethane methacrylate oligomer, acrylate monomer, filler, phosphine oxides, pigment, methacrylate monomer, phosphine oxide	NextDent	FDA-approved Class IIa CE certified[13]
Saremco print CROWNTEC (SA)	BisEMA, trimethylbenzoyldiphenylphosphine oxide	Saremco Dental AG	FDA-approved[b] Class IIa CE certified
Temp Print (TP)	Urethane dimethacrylate 50–<75%, 2,2′-ethylenedioxydiethyl dimethacrylate 10%<25%	GC	FDA-approved[c] Class IIa CE certified
3DELTA ETEMP (DM)	Methacrylates, urethane dimethacrylate, trimethylolpropane triacrylate, trimethylbenzoyl-diphenylphosphine oxide	Deltamed	No info available[d] Class IIa CE certified
MED690 (ST)	Acrylic monomer (<30%), 2-propenoic acid, 1,7,7-trimethylbicyclo[2.2.1] hept-2-yl ester, exo- (<25%), acrylic oligomer (<15%), photo initiator (<3%), titanium dioxide (<0.8%), acrylic acid ester (<0.3%), carbon black (0.1%-1%), xylenes (0.01%-0.1%), n-butyl acetate (0.01%-0.1%), ethylbenzene (0.01%-0.1%), propylene glycol monomethyl ether acetate (0.01%-0.1%), phosphoric acid (0.0005%-0.002%)	Stratasys, Ltd	No info available Class IIa CE certified
Gradia Direct (GR, GC)	Urethane dimethacrylate 10%-<25%, (octahydro-4,7-methano-1h-indenediyl)bis(methylene) bismethacrylate 2.5%-<5% and 2,2-dimethyl-1,3-propanediyl bismethacrylate 2.5%-<5%	GC	FDA-approved[e] Class IIa CE certified
Clearfil Majesty (CM)	Bisphenol a diglycidylmethacrylate (2.5%-10%), silanated barium glass filler, prepolymerized organic filler, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, DL-camphorquinone, accelerators, initiators, pigments	Kuraray Noritake	FDA-approved[f] Class IIa CE certified
Tetric EvoCeram (TE)	Urethane dimethacrylate (5%-10%), bis-GMA (3%-7%), ytterbium trifluoride (3%-5%), ethoxylated bisphenol a dimethacrylate (3%-5%)	Ivoclar Vivadent AG	FDA-approved[g] Class IIa CE certified
Gradia Direct Flo (GR-F, GC	Urethane dimethacrylate 25%–50%, dimethacrylate 5%-10%, and stabilizer <0.5%	GC	FDA-approved[h] Class IIa CE certified
Clearfil Majesty Flow (CM-F)	Triethylene glycol dimethacrylate<10%, hydrophobic aromatic dimethacrylate, silanated barium glass filler, silanated silica filler, DL-camphorquinone, accelerators, initiators	Kuraray Noritake	FDA-approved[i] Class IIa CE certified
Tetric EvoFlow (TE-F)	Bis-GMA (10%-25%), urethane dimethacrylate (10%-25%), ytterbium trifluoride (10%-25%), 1,10-decanediol dimethacrylate (2.5%-10%), diphenyl(2,4,6- trimethylbenzoyl)phosphine oxide (<2.5%), 2-(2-hydroxy-5-methylphenyl)-benzotriazol; 2-(2h-benzotriazol-2-yl)-p-kresol (<2.5%)	Ivoclar Vivadent AG	FDA-approved[j] Class IIa CE certified

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restorations, except for 1 material (Saremco print CROWNTEC; Saremco Dental AG) which was also marketed for definitive restorations. The conventional composite resins were marketed for definitive restorations. The null hypotheses were that the microhardness results would not be affected by the material type (high- and low-viscosity conventional and additively manufactured polymers) or the aging method.

MATERIAL AND METHODS

A flowchart of the experimental procedures is presented in Figure 1. Materials, their chemical compositions, and manufacturers are shown in Table 1.

Twenty Ø10×2-mm specimens from each composite resin system were manufactured in 2 increments from custom Teflon molds. The composite resins tested were either of low or high viscosity as specified in Table 1. A 1.1-mm glass slide and polyester strip were positioned at both ends of the mold and seated with finger pressure to extrude excess material and to obtain a flat surface. The specimens were subsequently kept dry and at room temperature. The surface of all specimens was polished (Struers) by using #1200 silicon carbide abrasive papers (Abramin; Struers) under constant irrigation for 10 seconds to obtain a flat surface, the thickness of which was verified by using digital micrometers (Mitutoyo).[25]

A standard tessellation language (STL) file of a Ø10×2-mm cylindrical design was obtained and processed by using a CAD software program (Modellier; Zirkonzahn). The STL file was exported and used to manufacture 20 specimens for each group (OP [Optiprint Temp; Dentona]; ND [C&B MFH; NextDent]; SA [Saremco print CROWNTEC; Saremco Dental AG]; TP [Temp Print; GC]; DM [3DELTA ETEMP; Deltamed]; ST [MED690; Stratasys, Ltd]) (Table 1). The specimens of all groups except ST were printed with a 3D printer (Asiga Max UV; Asiga) calibrated according to the standardized printing protocol for each material provided by the manufacturer. The group ST was processed with the PolyJet printing technology by using the corresponding printer (Stratasys J700; Stratasys, Ltd).

All printing parameters, such as the position of the build platform, printing thickness (50 μm), and orientation (round surface facing the build platform), were identical in all groups. The specimens were then removed from the build platform by using removal tools and submerged in an ultrasonic bath with 99% isopropyl alcohol for 5 minutes. After cleaning, the specimens were retrieved, dried, and polymerized in an ultraviolet (UV)-polymerization machine (Otoflash Post Curing Light Pulsing Unit; EnvisionTEC) with full spectrum (300 to 700 nm) for 10 minutes. The sample size was determined according to a previous study.[14] The surface of all specimens was polished by using the #1200 silicon carbide abrasive paper in a metal device under constant water irrigation for 10 seconds to obtain a flat stable surface and verified by using the digital micrometer as for the conventional polymers.[25]

Before microhardness testing, the specimens of each group were randomly attributed to 2 different aging procedures, either nonaging or aging (n=10 per group), by using a shuffled deck of cards. In the aging groups, the specimens underwent 6000 cycles of thermocycling (5 °C to 55 °C) consisting of 3 steps each: 20 seconds (dwell time) at 5 °C; 5 seconds (transfer time) at 23 °C; 20 seconds (dwell time) at 55 °C.[26] The nonaged groups were kept dry at room temperature (23 °C) before testing.

The Vickers hardness (VH) was measured (ZHV30; Zwick) on the polymeric specimens according to International Organization for Standardization (ISO) 6507.[23] Three indentations were made on each specimen with a 0.98-N load for 15 seconds, and measurements were conducted on the surface of each specimen. The mean value of microhardness of all 3 measurements for each specimen was used for statistical analysis.[27]

Statistical analyses were performed by using a statistical software package (IBM SPSS Statistics for Windows, v26; IBM Corp). Data for the measurement parameter microhardness were analyzed in regard to polymer type and aging method by using the 2-way repeated measurement analysis of variance (ANOVA) and Tukey post hoc tests, depending on the normal distribution of the data (α=.05 for all tests). The maximum likelihood estimation of the 2-parameter Weibull distribution, by following the Anderson-Darling tests, without a correction factor, and including the Weibull modulus, scale (m) and shape (0), was used to interpret the predictability and reliability of the effect of material type and aging method on VH (Minitab Software V.16; Minitab).[28]

RESULTS

The 2 investigated parameters, material type and aging method, were evaluated separately and in correlation with each other. The statistical analysis revealed that the interaction of the parameters was not significant (P>.05).

While the material type presented a significant effect on the Vickers hardness (VH) results (P<.001), no difference was found when nonaged and aged groups were compared (P>.05).

Of all the material types, group ST (68 ±0.5 VHN) presented the highest mean values for microhardness, and group CM-F (17 ±0.5 VHN) the lowest. The remaining groups showed intermediate values in the following order: ST^{a}<OP^{b}, ND^{b}<SA^{c}, TP^{c}<GR^{d}, GR-F^{d}<DM^{e}, TE-F^{e}<CM^{f}<TE^{g}<CM-F^{h} (groups with different superscripts were significantly different from each other) (Fig. 2).

The VH results comparing the aged (37 ±1 VHN) and nonaged (35 ±1 VHN) specimens were not significantly different (P>.05). The percentage difference presented a higher mean of VH values for the aged groups except for the 3D polymer groups TP and ST and the conventional groups GR and CM (Figs. 3 and 4).

The Weibull distribution (Fig. 5), including the Anderson-Darling test results (AD; P), revealed statistically nonsignificant shape values for the highest (AD: 0.444) and lowest (AD: 0.653) shape values of the aged and nonaged groups (P>.05).

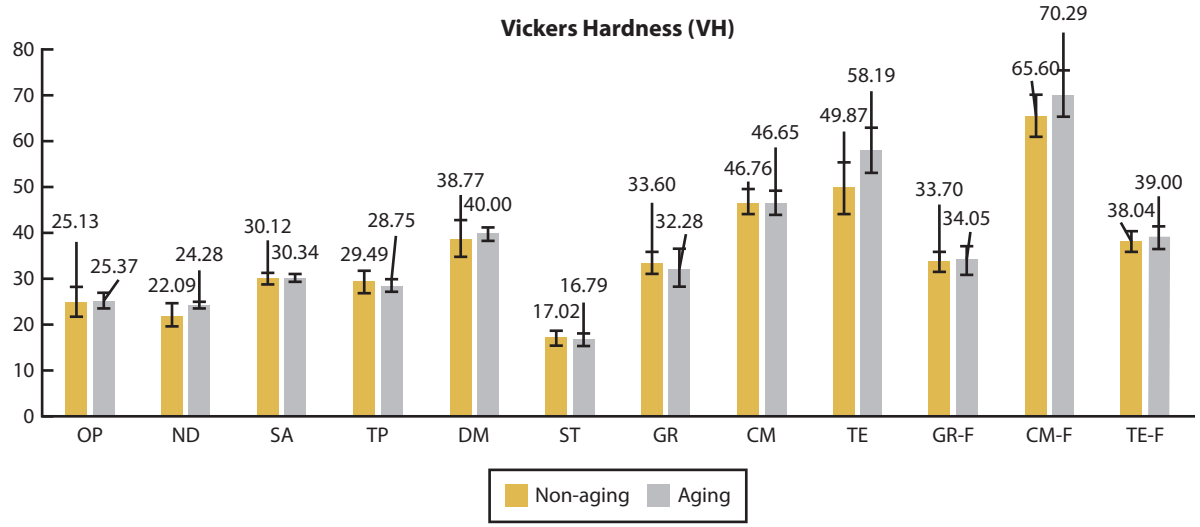


Figure 2. Mean and standard deviation of Vickers hardness values of aged and nonaged specimens of composite resins tested (Optiprint temp [OP]; C&B MFH [ND]; Saremco print CROWNTEC [SA]; Temp Print [TP]; 3DELTA ETEMP [DM]; MED690 [ST], Gradia Direct [GR]; Clearfil Majesty [CM]; Tetric EvoCeram [TE]) and high Gradia Direct Flo (GR-F); Clearfil Majesty Flow (CM-F); Tetric EvoFlow (TE-F). x axis indicates Vickers Hardness (VH); y axis indicates tested materials.

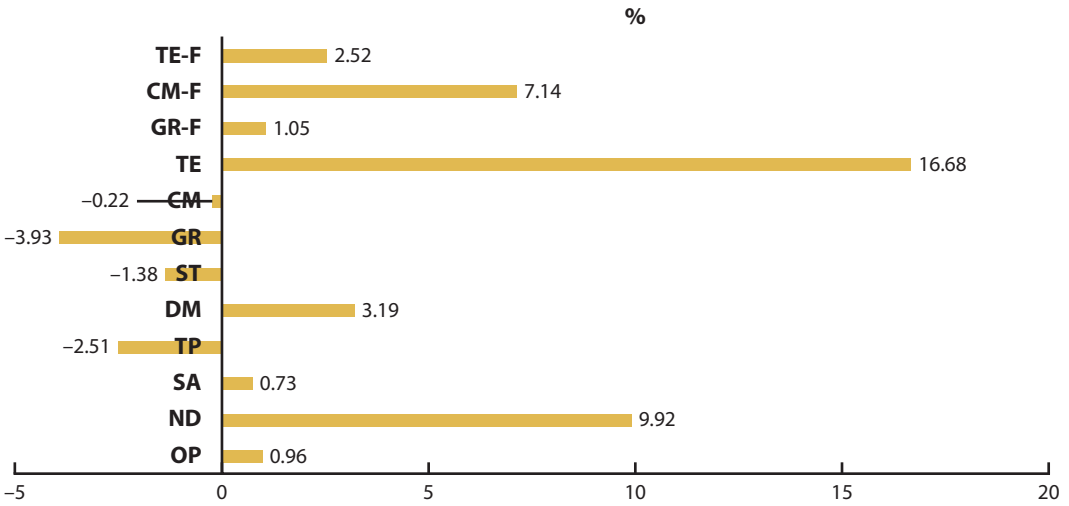


Figure 3. Percentage difference of aged and nonaged mean Vickers hardness values of specimens of composite resins tested. CM, Clearfil Majesty; CM-F, Clearfil Majesty Flow; DM, 3DELTA ETEMP; GR, Gradia Direct; GR-F, Gradia Direct Flo; ND, C&B MFH; OP, Optiprint temp; SA, Saremco print CROWNTEC; ST, MED690; TE, Tetric EvoCeram; TE-F, Tetric EvoFlow; TP, Temp Print. x axis indicates percentage (%) difference of aged and nonaged mean Vickers Hardness (VH); y axis indicates tested materials.

DISCUSSION

This in vitro study was undertaken to assess the effect of hydrothermal aging on the Vickers hardness of low- and high-viscosity conventional and additively manufactured polymers. The first null hypothesis was rejected, as the material type showed significant differences when mean microhardness values were compared, while the second null hypothesis for the aging method was accepted. The interaction between the parameters "material type" and "aging" was also not significant.

The mechanical performance of additively manufactured polymers has not yet been studied thoroughly. Microhardness does not only dictate the esthetic appearance but also influence plaque accumulation, carious lesion formation, and the abrasion behavior of restorative materials. Ideal hardness is also necessary to maintain anatomic form and stability to withstand flexural stresses caused by mastication forces in the oral environment.[19] However, viscosity and the speed of the polymerization process are important parameters of the

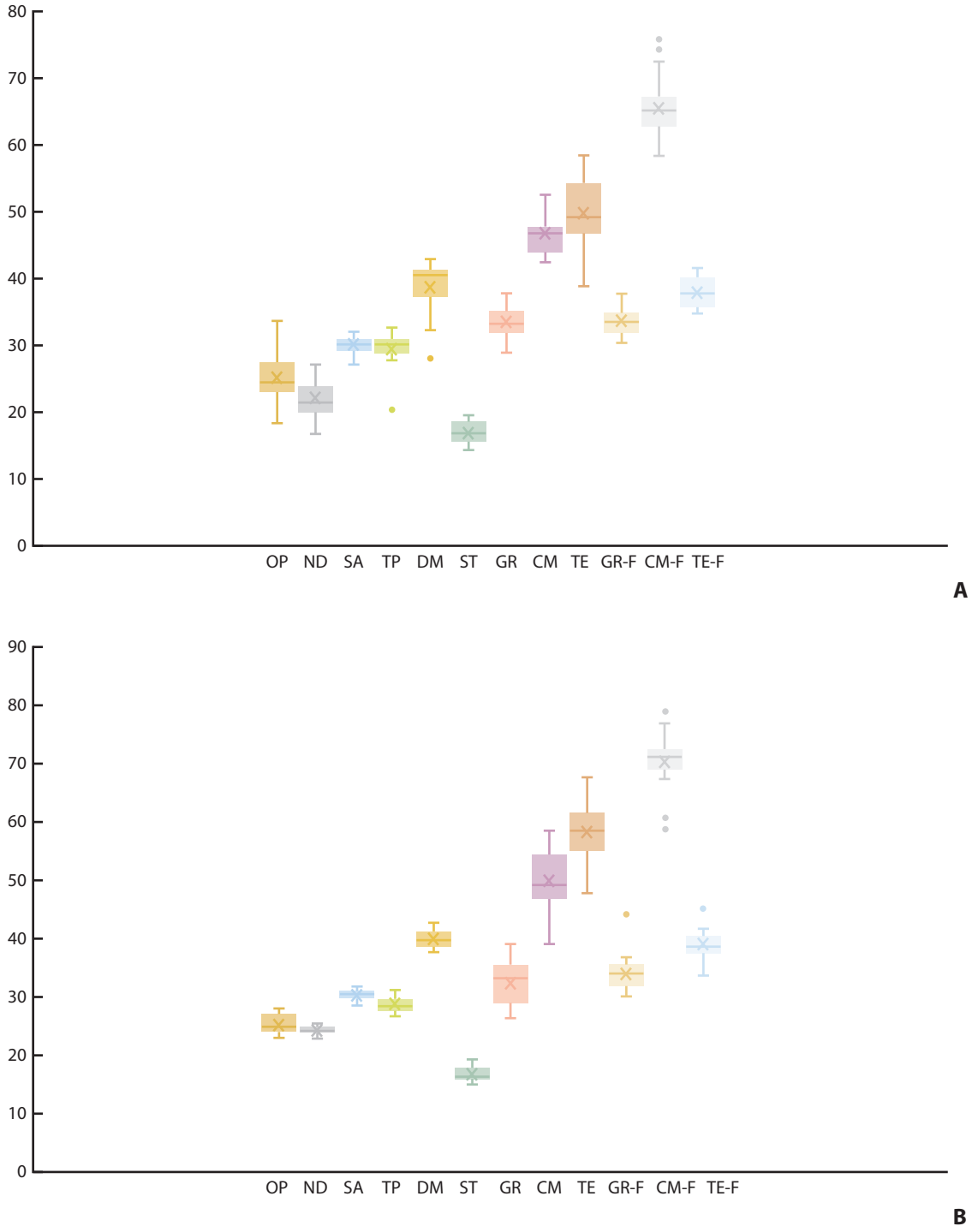
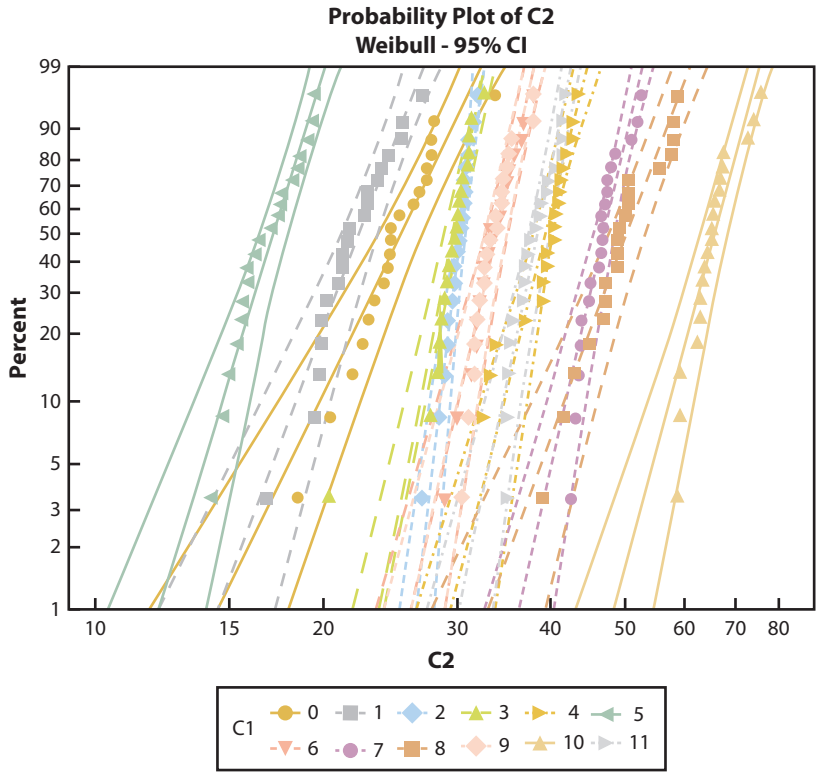


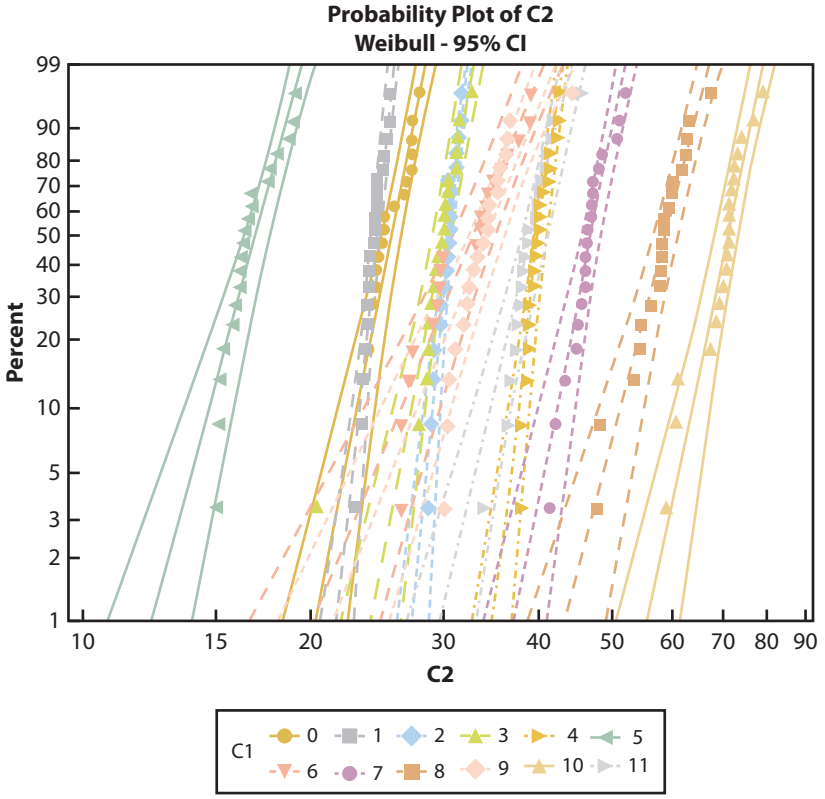
Figure 4. Box plot of Vickers hardness (VH) values for specimens of composite resins tested. A, Nonaged. B, Aged. CM, Clearfil Majesty; CM-F, Clearfil Majesty Flow; DM, 3DELTA ETEMP; GR, Gradia Direct; GR-F, Gradia Direct Flo; ND, C&B MFH; OP, Optiprint temp; SA, Saremco print CROWNTEC; ST, MED690; TE, Tetric EvoCeram; TE-F, Tetric EvoFlow; TP, Temp Print. x axis indicates tested materials.

dental polymers. While viscosity should not be too low or too high, the residual monomer concentration should not be reduced by using higher amounts of photoinitiators to accelerate polymerization.[9] Therefore, additively manufactured polymers were compared with low- and high-viscosity composite resins in the present study, with additively manufactured polymers showing similar viscosity values to high-viscosity composite resins.



Shape	Scale	N	AD	P
7.673	26.56	20	0.653	.081
9.803	23.18	20	0.366	>.250
32.77	30.63	20	0.143	>.250
19.65	30.34	20	0.564	.144
15.04	40.31	20	0.804	.033
11.98	17.75	20	0.445	>.250
16.49	34.64	20	0.272	>.250
16.42	48.12	20	0.853	.024
10.02	52.34	20	0.764	.042
16.53	34.66	20	0.736	.047
13.92	67.79	20	1.055	<.010
18.13	39.13	20	0.631	.091

A



Shape	Scale	N	AD	P
18.01	26.10	20	0.814	.030
36.07	24.62	20	0.590	.119
37.81	30.78	20	0.444	>.250
19.65	30.34	20	0.564	.144
28.94	40.70	20	0.584	.125
13.27	17.39	20	0.904	.019
8.870	34.09	20	0.456	.248
18.03	47.92	20	0.847	.024
14.11	60.29	20	0.331	>.250
9.106	35.57	20	1.434	<.010
17.56	72.42	20	0.796	.034
15.29	40.15	20	0.787	.037

B

Figure 5. Two-parameter Weibull modulus distribution for specimens of composite resins tested. A, Nonaged. B, Aged. Optiprint temp (0); C&B MFH (1); Saremco print CROWNTEC (2); Temp Print (3); 3DELTA ETEMP (4); MED690 (5), or conventional low (Gradia Direct [6]; Clearfil Majesty [7]; Tetric EvoCeram [8]) and high (Gradia Direct Flo [9]; Clearfil Majesty Flow [10]; Tetric EvoFlow [11]).

Once a dental restoration is placed, its long-term survival is influenced by parameters that include the selected material type, the skill of the dentist, and the compliance of the patient.[22] Usually, the volumetric polymerization shrinkage of composite resins, even in ideal conditions, ranges between 1% and 4.8% depending on the presence of dimethacrylates and the volume percentage of inorganic fillers.[21] As the composition of the polymers influences the shrinkage behavior, various additively manufactured polymers with varying compositions were selected for the present study.

Recently, additive manufacturing technologies (3D printing) have introduced new polymers, including the manufacturer Dentona with the product OP (a mixture of bis-EMA and dimethylacrylate); NextDent with the product ND (methacrylic oligomers, methacrylate monomer, inorganic urethane methacrylate oligomer); Saremco Dental AG with the product SA (mixture of bis-EMA and trimethylbenzoyldiphenylphosphine oxide); GC with the product TP (urethane dimethacrylate, 2,2′-ethylenedioxydiethyl dimethacrylate); Deltamed with the product DM (methacrylates, urethane dimethacrylate); and Stratasys with ST (acrylic monomers, 2-propenoic acid, 1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, exo-, acrylic oligomer) for potential use in medical and dental applications. The integration of urethane dimethacrylates alone in the additively manufactured polymers, as in groups ND, TP, and DM, does not ensure high microhardness, but the interaction with the other components seems to strongly influence the Vickers hardness of the additively manufactured polymers.

The conventional material groups GR and GR-F consisted mainly of urethane dimethacrylates; the groups TE and TE-Flow consisted of a mixture of Bis-GMA and urethane dimethacrylates. The integration of triethylene glycol dimethacrylate (TEGDMA) in the CM-F group or a mixture of bis-GMA and urethane dimethacrylates in the TE and TE-F groups seems to be favorable according to the Vickers hardness.

The testing of the aged groups was an attempt to simulate intraoral clinical conditions. Water storage and thermocycling have been the most accepted techniques for in vitro studies,[26] and thermocycling was used in the present study. Unlike in the present study, Badra et al[19] reported that Vickers hardness was influenced by aging procedures, including in water, in alcohol, and exposure to UV radiation. However, Badra et al[19] also stored specimens in acids, not done in the present study.

Chladek et al[20] reported that high temperatures decrease the physical and chemical properties of composite resins by reducing the number of unreacted double bonds. In the present study, the Vickers hardness values in the aged (37 ±1 VHN) and nonaged (35 ±1 VHN) specimens were not statistically different ($P>.05$) (Fig. 3). The similar values could be because of heat-induced additional polymerization, increasing the degree of conversion, which may have been equivalent to the reduction of the number of unreacted double bonds. Furthermore, the Weibull distribution presented slightly more reliable results with the aged groups than with the nonaged groups when additively manufactured polymers were evaluated.

Limitations of the study included the in vitro design that did not include saliva or masticatory forces. While material printing parameters and postprocessing procedures were followed according to the specific protocols of the manufacturers, the final polishing was standardized to create equal conditions for the materials tested. However, not all specimens were fabricated by using the same printer and printer technologies, as the ST group required PolyJet printing technologies and could not be processed by using the digital light projector (DLP) technology. Future investigations should measure the viscosity of the materials and evaluate the microhardness of additively manufactured polymers by using larger sample sizes.

CONCLUSIONS

Based on the findings of this in vitro study, the following conclusions were drawn:

1. The polymeric material types tested significantly affected the hardness values, where a lower Vickers hardness was obtained for the 3D-printed materials that for those of conventional composite resins.
2. The material type was not affected by aging conditions when compared with their nonaged control groups.

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