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Filler Content, Surface Microhardness, and Rheological Properties of Various Flowable Resin Composites

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Clinical Relevance Statement

Using a flowable resin composite with high filler content, high initial surface microhardness, low viscosity, and good spreadability may be a satisfactory clinical compromise between mechanical properties and ease of use for the restoration of low-volume cavities.

SUMMARY

Objectives: The objectives of this study were to determine the filler content, the surface microhardness (at baseline and after immersion in water for 2 years), and the rheological properties of various flowable resin composites.

Methods: Three flowable resin composites (Grandioso Heavy Flow [GHF], Grandio Flow [GRF], Filtek Supreme XTE Flow [XTE]), one pit and fissure sealant resin composite (Clin-Pro [CLI]), and three experimental flowable resin composites with the same matrix and a variable filler content (EXPA, EXPB, EXPC) were tested. The filler content was determined by calcination. The Vickers surface microhardness was determined after polymerization and then after immersion in distilled water at 37°C for 7, 60, 180, 360, and 720 days. The rheological measurements were performed using a dynamic shear rheometer.

Results: The determined filler contents differed from the manufacturers' data for all the materials. The materials with the highest filler content presented the highest microhardness, but filler content did not appear to be the only influencing parameter. With respect to the values recorded after photopolymerization, the values were maintained or increased after 720 days compared with the initial microhardness values, except for GHF. For the values measured after immersion for 7 days, an increase in microhardness was observed for all the materials over time. All the materials were non-Newtonian, with shear-thinning behavior. At all the shear speeds, GRF presented a lower viscosity to GHF and XTE.

Conclusions: GRF presented a low viscosity before photopolymerization, associated with high filler content, thereby providing a good compromise between spreadability and mechanical properties after photopolymerization.

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DOI: 10.2341/16-031-L

INTRODUCTION

Preventive dentistry, adhesive dentistry, and ultraconservative dentistry have all developed significantly in recent decades and are now an integral part of the treatment arsenal available to practitioners. In the past 15 or so years, the emergence of flowable resin composites has further expanded the range of options available to dentists.[1,2] The relative ease of use of these low-viscosity resins, their capacity to spread and take shape in small occlusal or cervical cavities, as well as their ability to penetrate into pits and fissures mean that they have been adopted by numerous dental practitioners.[3-5] Inside the warm, moist environment of the mouth, materials which are subject to abrasion and numerous mechanical stresses, particularly flexion and compression, need to meet a broad range of specifications to ensure long-term clinical success. From this point of view, *in vitro* study of the physical and mechanical properties of materials is essential since it helps evaluate the capacity of materials to meet said specifications. One of the most useful properties to assess is the surface microhardness because this is closely correlated with resistance to compression and resistance to abrasion,[6-9] parameters that are particularly important, especially when the materials are used in low thicknesses, as is frequently the case for low-viscosity "flowable" resin composites. For the latter, it is important to specify that to make a resin composite flowable, manufacturers can primarily intervene on two levels. The first option consists of increasing the proportion of viscosity-lowering monomers to counter the high viscosity of high-molecular-weight monomers such as bisphenol A glycidyl dimethacrylate (Bis-GMA). These viscosity-lowering monomers are small, low molecular weight aliphatic monomers; triethylene glycol dimethacrylate (TEGDMA) is very frequently used for this purpose, for example. The second option consists of reducing the filler content in terms of volume compared with the matrix volume. Obviously, the two options can be employed simultaneously to varying degrees. These specific composition characteristics will therefore influence the initial viscosity of these resin composites, as well as their physical and mechanical properties once they are photopolymerized.

The literature available concerning the microhardness of resin composites is relatively abundant, but the study protocols used are highly variable, making comparison between them difficult.[10-15] In addition, to date, no study has described the evolution of microhardness after more than 6 months of immersion in a medium simulating the oral cavity, meaning that its long-term evolution has been little reported. Furthermore, the notion of resin viscosity remains somewhat vague, with the term *flowable* simply an indication used by manufacturers to cover a group of nonetheless very different materials.

The objectives of our study were as follows: 1) to determine the filler content of various flowable resin composites, 2) to determine the initial surface microhardness, 3) to monitor the evolution in surface microhardness following immersion in distilled water for 2 years, and finally, 4) to determine the rheological properties of various flowable resin composites. To perform this study, three commercially available flowable resin composites and one ultra-flowable resin pit and fissure sealant, along with three experimental flowable resin composites, were used.

METHODS AND MATERIALS

The compositions of the products used are presented in Table 1. Three flowable resin composites (Grandio Flow and GrandioSo Heavy Flow, Voco, Cuhaven, Germany; Filtek Supreme XTE flow, 3M ESPE Dental Products, St Paul, MN, USA), one ultra-flowable resin pit and fissure sealant material (Clinpro Sealant, 3M ESPE Dental Products), and three experimental flowable resin composites with the same matrix and a variable filler content were used. The experimental resin composites were manufactured at our request by Voco. The decision to include experimental materials among the materials studied was guided by a desire to exclude the "matrix" parameter to record the influence of the filler content alone. The decision to include an ultra-flowable pit and fissure sealant resin among the materials studied was guided by a desire to record the potential impact of the absence of fillers, since ClinPro (CLI) is described as unfilled by the manufacturer.

In total, 56 disc-shaped specimens were prepared; eight disks of each material were made. The samples were prepared using a Teflon mold (15 mm in diameter by 1 mm in thickness). For each sample, the material was injected into the mold using an applicator nozzle, remaining in contact with one wall of the mold to minimize air inclusion. A glass slide with a thickness of 1.10 mm was then firmly applied and held on the mold using a clamp to compress the material and eliminate any excess. Polymerization was performed using a light-emitting diode lamp

Table 1: *Materials Used in This Study*

Code	Material (Manufacturer)	Main Components	Shade	Batch No.
GHF	Grandio So Heavy Flow (Voco D-27457 Cuxhafen Germany)	*Monomers:* Bis-GMA, Bis-EMA, TEGDMA *Fillers: (83 wt.% = 68 vol.%):* glass ceramic (average particle size: 1 μm), functionalized SiO_2 nanoparticles (from 20 to 40 nm)	A3	1234322
GRF	Grandio Flow (Voco D-27457 Cuxhafen Germany)	*Monomers:* Bis-GMA, HEDMA, TEGDMA *Fillers: (80.2 wt.% = 65.7 vol.%):* nano-hybrid inorganic fillers	A3	1233159
XTE	Filtek Supreme XTE Flow (3M/ESPE Dental Products St Paul, MI, USA)	*Monomers:* Bis-GMA, TEGDMA, Procrylat resins *Fillers: (65 wt.% =46 vol.%):* ytterbium trifluoride (from 0.1 to 5.0 μm), nonagglomerated/nonaggregated surface modified 20-nm silica fillers, nonagglomerated/nonaggregated surface-modified 75-nm silica fillers, surface-modified aggregated zirconia/silica fillers (composed of 20-nm and 4- to 11-nm zirconia particles with an average cluster particle size of 0.6 to 10 μm)	A3	N412976
CLI	Clinpro Sealant (3M/ESPE Dental Products, St Paul, MI, USA)	*Monomers:* Bis-GMA, TEGDMA *Fillers:* unfilled	—	N401833
EXPA	Experimental RBC (Voco D-27457, Cuxhafen, Germany)	*Monomers:* Bis-GMA (33wt.%), UDMA (33 wt.%), TEGDMA(33 wt.%) *Fillers: (65 wt.%):* silanized glass, silica (7 μm)	A3	—
EXPB	Experimental RBC (Voco D-27457, Cuxhafen, Germany)	*Monomers:* Bis-GMA (33wt.%), UDMA (33 wt.%), TEGDMA(33 wt.%) *Fillers: (55 wt.%):* silanized glass, silica (7 μm)	A3	—
EXPC	Experimental RBC (Voco D-27457, Cuxhafen, Germany)	*Monomers:* Bis-GMA (33 wt.%), UDMA (33 wt.%), TEGDMA (33 wt.%) *Fillers: (45 wt.%):* silanized glass, silica (7 μm)	A3	—

Abbreviations: Bis-EMA, ethoxylated bisphenol-A glycol dimethacrylate; Bis-GMA, bisphenol-A glycidylmethacrylate; HEDMA, hexanediol dimethacrylate; RBC, resin-based composite; TEGDMA, triethyleneglycol dimethacrylate; UDMA, urethane dimethacrylate.

(Elipar Freelight 2, 3M ESPE Dental Products). The light tip was first directed over the center of the sample for 40 seconds and then irradiated eight peripheral overlapping sectors for 20 seconds each. The samples were then carefully removed from the molds. The side opposite the one already photopolymerized was also exposed in the same way. Each sample was thus photopolymerized for a total of 400 seconds. Excess material was carefully removed using a scalpel blade.

Determination of the Filler Content Mass by Calcination

Three samples of each of the materials taken using the protocol described previously were weighed on a precision balance (Précisa, XB220A, Dietikon, Switzerland) to determine their initial mass. The samples were then placed in a chamber furnace with a power of 10 kW^2 (Nabertherm, LH30/14, Lilienthal, Germany) and heated to a temperature of 900°C for one hour. They were gradually returned to room temperature simply by stopping the heating cycle. Calcining the materials led to elimination of the resin matrix, leaving only the fillers in the form of an agglomerated residual powder. The calcination residue was then weighed. The filler content by mass, as a percentage, was determined using the formula (residue mass/initial mass of samples before calcination) × 100.

Microhardness Assessment

Five samples of each of the materials prepared using the protocol described above were tested. The initial microhardness of the samples was determined immediately after preparation using a microhardness tester (Matsuzawa MXT 50, Matsuzawa Seiki Co Ltd, Tokyo, Japan). A 200-g weight was applied for 20 seconds to the side to be polymerized first through the glass slide. The diagonals of the square imprint left by the diamond pyramid tip were measured after positioning cursors on a monitor (Ryokosha Co Ltd, Tokyo, Japan) coupled to the indentation hardness meter, with a magnification of 400×. The Vickers microhardness was obtained using the following formula: $VHN = (1854.4 \times W)/d^2$ (where VHN is the Vickers hardness number expressed in kg/mm^2, W is the weight in g, and d is the length of the diagonal in μm). Three measurements at different randomly selected points were performed per sample. After measurement, the samples were immediately stored in distilled water and placed in an oven at 37°C (Firlabo, Meyzieu, France). After 7 days, 60 days (2 months), 180 days (6 months), 360 days (1 year), and 720 days (2 years), each sample was briefly rinsed with distilled water, carefully wiped using absorbent paper, and left in air for 15 seconds before the microhardness was tested again at three different randomly chosen points, all on the same side. The distilled water storage

Table 2: *Filler Content by Mass as a Percentage for the Different Materials Tested*

Material	Wt.% (SD)
GHF	78.6 (0.1)
GRF	77.3 (0.1)
XTE	58.9 (0.2)
CLI	26.5 (0.8)
EXPA	63.1 (1.6)
EXPB	53.7 (0.2)
EXPC	43.6 (0.1)

medium was changed every 15 days for two years. The results were statistically analyzed using Kruskal-Wallis tests followed by paired multiple comparisons (Bonferroni adjustment; $\alpha=0.05$).

Rheological Properties

A dynamic shear rheometer (Physica MCR 301, Anton Paar GmbH, Graz, Austria) connected to a temperature control system (TC30, Anton Paar GmbH) was used to determine the rheological properties of the materials tested. A parallel plate viscometer module with a diameter of 25 mm was used. The gap between the plates was 1 mm. The temperature in the chamber was controlled at 23°C. Given the thixotropic behavior of resin composites, a preshear test was performed at a speed of 1 s^{-1} over 360° before a sweep test at a constant frequency of 0.1 $rad.s^{-1}$ for 7200 seconds. Then the sweep test was performed at an angular frequency of 100 to 0.01 $rad.s^{-1}$, making it possible to determine, due to sinusoidal strain, the viscosity (Pa.s) and the elastic storage modulus G' (Pa) as a function of the shear frequency imposed.

RESULTS

The results of the determination of the filler content using the calcination method are presented in Table 2. The filler contents can be ranked in decreasing order as follows: Grandioso Heavy Flow (GHF), Grandio Flow (GRF), Filtek Supreme XTE Flow (XTE), and CLI for the commercially available materials and EXPA, EXPB, and EXPC for the experimental materials.

The results for determination of microhardness are presented in Tables 3 and 4. Before immersion, the commercially available materials tested presented significantly different microhardnesses ($p<0.0001$), with, in decreasing order, GHF, GRF, XTE, then CLI. For GHF and GRF, a significant decrease in the values was observed after seven days of immersion ($p<0.0001$), which is not the case for XTE and CLI. After 2 years of immersion, CLI and XTE present, on average, hardness values that are significantly higher than the initial values ($p<0.0001$), whereas GRF presents average hardness values that are not significantly different from the initial values and GHF presents average values that are significantly lower than the initial values ($p<0.0001$).

Irrespective of the immersion time, the experimental materials tested presented significantly different microhardness ($p<0.0001$), with, in decreasing order, EXPA, EXPB, and EXPC. After two years of immersion, the three experimental materials presented, on average, hardness values that were significantly higher than the initial values ($p<0.0001$).

The curves for complex viscosity and storage modulus as a function of shear frequency for the commercially available materials tested are presented in Figures 1 and 2; those for the experimental materials tested are presented in Figures 3 and 4. For all materials, the viscosity decreased as the shear frequency increased. Irrespective of the shear frequency, the viscosity can be ranked in decreasing order as follows: GHF, GRF, XTE, and CLI for the commercially available materials and EXPA, EXPB, and EXPC for the experimental materials. For all the materials, the storage modulus increased as the frequency increased. Irrespective of the shear fre-

Table 3: *Evolution of Vickers Microhardness Mean Values (Standard Deviation) for the Different Commercially Available Materials Tested as a Function of Their Immersion Time in Distilled Water*[a]

Material	Immediately Postcure	Immersion Time					
	J0	J7	J60	J120	J180	J360	J720
GHF	68.0^{aA} (1.9)	58.0^{aB} (1.7)	61.7^{aC} (1.1)	62.9^{aC} (1.6)	62.7^{aC} (1.27)	63.5^{aC} (2.6)	63.3^{aC} (1.4)
GRF	45.2^{bA} (2.3)	40.9^{bB} (1.4)	41.8^{bA} (1.0)	42.0^{bA} (1.3)	42.37^{bA} (1.1)	42.4^{bA} (1.0)	43.5^{bA} (1.3)
XTE	36.3^{cA} (2.0)	37.9^{bA} (1.2)	38.6^{cA} (1.0)	39.9^{bA} (1.4)	38.9^{cA} (0.8)	41.0^{bB} (0.6)	41.7^{bB} (0.7)
CLI	9.5^{dA} (0.6)	9.5^{cA} (0.5)	10.4^{dB} (0.2)	10.9^{cB} (0.3)	10.9^{dB} (0.2)	11.6^{cC} (0.1)	12.3^{cC} (0.2)

[a] *In each column, results with the same superscript lowercase letter are not statistically different. In each row, results with the same superscript uppercase letter are not statistically different.*

Table 4: *Evolution of Vickers Microhardness Mean Values (Standard Deviation) for the Different Experimental Materials Tested as a Function of Their Immersion Time in Distilled Water*[a]

Material	Immediately Postcure	Immersion Time					
	J0	J7	J60	J120	J180	J360	J720
EXPA	32.2^{aA} (1.3)	31.3^{aA} (0.8)	34.8^{aB} (0.6)	34.4^{aB} (0.7)	34.1^{aB} (0.7)	34.8^{aB} (1.0)	34.7^{aB} (0.4)
EXPB	23.6^{bA} (0.8)	24.4^{bA} (1.2)	24.6^{bA} (0.3)	25.6^{bA} (0.6)	25.2^{bA} (0.3)	26.0^{bB} (0.4)	27.2^{bC} (0.3)
EXPC	18.9^{cA} (0.6)	19.3^{cA} (0.4)	21.5^{cB} (0.3)	21.5^{cB} (0.5)	21.6^{cB} (0.5)	21.6^{cB} (0.3)	22.3^{cC} (0.3)

[a] *In each column, results with the same superscript lowercase letter are not statistically different. In each row, results with the same superscript uppercase letter are not statistically different.*

quency, the storage modulus can be ranked in decreasing order as follows: XTE, GHF, GRF, and CLI for the commercially available materials and EXPA, EXPB, and EXPC for the experimental materials.

DISCUSSION

It is widely accepted that the higher the filler content of a resin composite, the better its mechanical behavior and, consequently, the greater the potential durability of the restoration made using

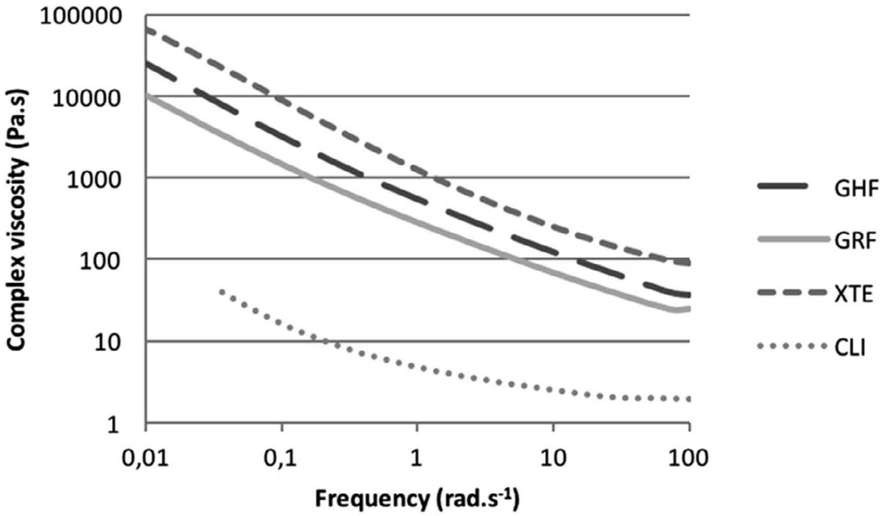

Fig 1

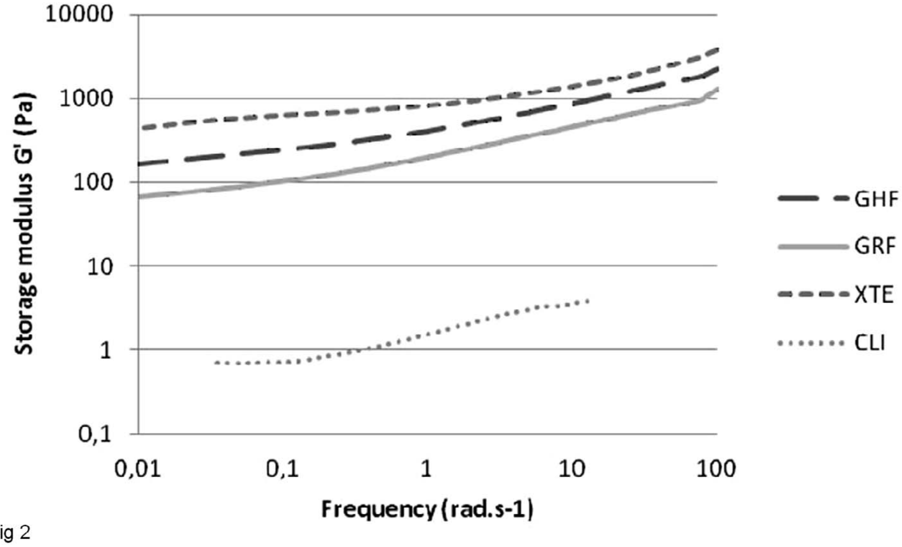

Fig 2

Figure 1. *Complex viscosity of the commercially available materials as a function of shear frequency.*
Figure 2. *Storage modulus G′ of the commercially available materials as a function of shear frequency.*

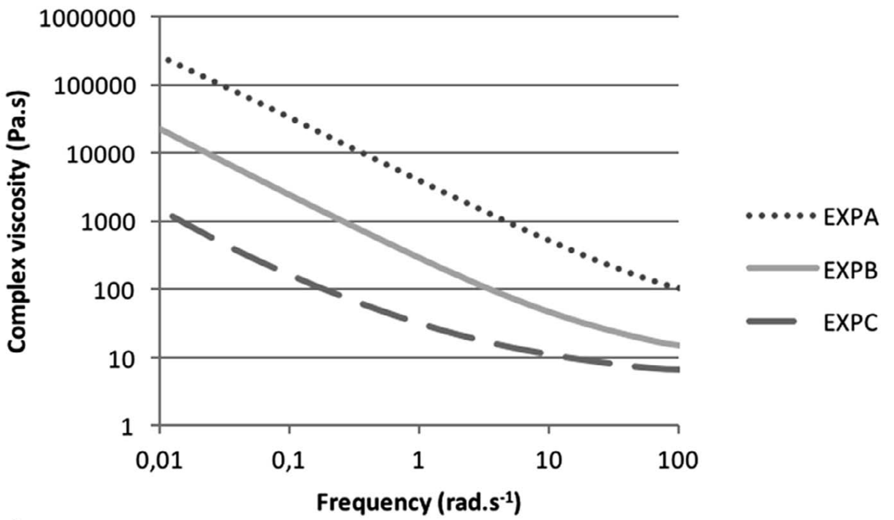

Fig 3

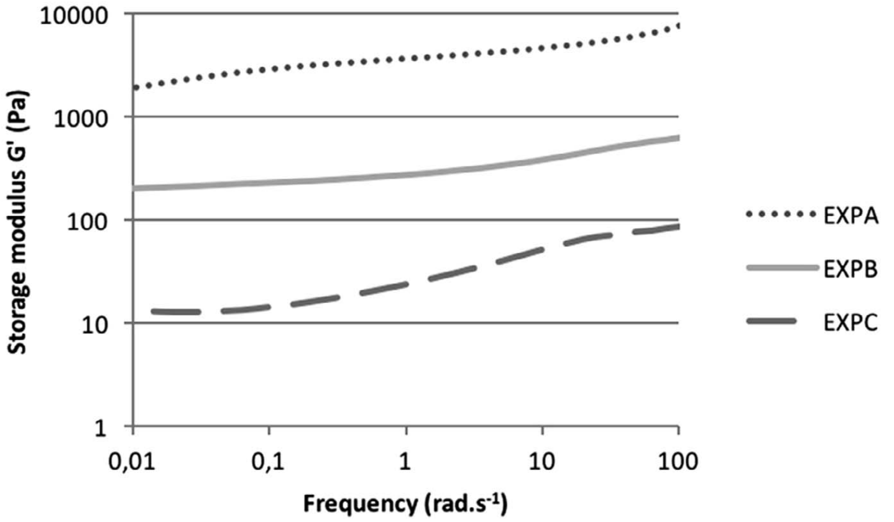

Fig 4

Figure 3. *Complex viscosity of the experimental materials as a function of shear frequency.*

Figure 4. *Storage modulus G′ of the experimental materials as a function of shear frequency.*

said resin composite.[16-18] As a result, the filler content is sometimes highlighted by manufacturers as a commercial argument, and resin composites with a very high filler content have emerged.[18,19] But to make a resin composite more flowable, one of the methods commonly used by manufacturers consists in reducing the filler content, thereby potentially affecting its mechanical properties. Nonetheless, resin composites described as both flowable and having high filler content have appeared on the market.

Our values for filler content by weight do indeed indicate high values for GHF and GRF, of 78.6% and 77.3%, respectively. It is no surprise that, in contrast, CLI, intended as a pit and fissure sealant only, presents the lowest filler content, at 26.5 wt.%. The values obtained in our study do not entirely match the data supplied by manufacturers. Yet the calcination method used here, with heating to 900°C for one hour, effectively eliminates the organic portion of resin composites and appears to be a validated method, like thermogravimetric analysis, for determination of filler content.[20,21] The difference in value can probably be explained by the fact that manufacturers assess the filler content after silanization of the fillers. Silanization, which is essential for coupling between fillers and the matrix, involves industrial processes specific to each manufacturer, and the silane quantity used, as well as the thickness of the silane layer coating the fillers, depend on the methods used. If it is taken into account by the manufacturer when assessing the filler mass, this silane quantity increases the values, while, since it is eliminated during calcination, it is not taken into account in the measurements performed in our study. Similarly, the combination of small-sized mineral fillers in a prepolymerized resin matrix for the purposes of forming clusters of fillers with a higher diameter may explain the differences between our values and the manufacturer's data. In fact, the organic part of these fillers will be eliminated during calcination, whereas the mineral part will persist.[21] This destruction of the organic fraction of the fillers probably largely explains the difference in the values observed for XTE, described as containing 20 nm silica and 4 to 11 nm zirconia fillers grouped into clusters of 0.6 to 10 μm. For CLI, we determined a filler content of approximately 26 wt%. Surprisingly, the instructions for use accompanying CLI describe it as unfilled. However, oddly, the technical product profile available on request from the manufacturer specifies the presence of silanized amorphous silica fillers of 0.016 μm at a concentration of 6%, with no mass or volume indication relative to these data. It should be noted that the presence of TiO_2, which gives the material a white color after photopolymerization and is resistant to temperatures of 900°C, can also increase the mass of the residue after calcination, in line with the difference in values that exists between our measurements and the manufacturer's data. It therefore appears that, due to a lack of standardization in filler content determination methods, the values communicated by manufacturers should be regarded with a certain degree of caution.

Because it is a good indirect indicator of the mechanical performance of materials, surface microhardness is regularly used in studies.[15] In our study, the results obtained before immersion in distilled water for each of our materials—either commercially available or experimental—are consistent with the literature: the higher the filler content of a resin composite, the higher its surface microhardness.[22] It is no surprise that EXPA, with a filler content of 65 wt%, has the highest initial hardness of the experimental materials. Nor is it surprising that CLI, a material with an indication limited to pit and fissure sealing and with very low filler content, presents an initial surface microhardness that is about seven times lower than GHF, the material with the highest filler content in our study. However, given the nonlinear relationship observed between it and the values obtained, the filler content parameter alone is not the only explanation. For example, GHF and GRF, which have almost the same filler contents, present significant differences in terms of surface microhardness. This can probably be explained by the nature and proportion of the monomers included in the polymer network. The degree of cross-link density and the three-dimensional complexity appear to be factors with a major influence on the mechanical behavior of the polymer network.[23] Hence, small aliphatic monomers, such as TEGDMA, promote the formation of dense molecular networks;[24] BisGMA potentially leads to a lower conversion rate and a lower cross-link density,[25,26] but, conversely, due to its intrinsically rigid molecular structure and capacity to form hydrogen bonds between the monomers, it appears to be a pillar that supports the three-dimensional configuration of the polymer structure.[25,27] BisEMA, which is devoid of hydroxyl radicals but has a high molecular weight, potentially reduces the cross-link density of the polymer.[24] The BisGMA/TEGDMA combination, due to the presence of three ether bonds on the latter, appears to have a synergistic effect that increases the polymer network density.[27] Each monomer and each group therefore involves different properties and different molecular architectures.[20,28] But the absence of data supplied by manufacturers concerning the exact proportions of the different monomers makes interpretation of the current results complicated. What mainly emerges is that the filler content—even when very high—is not, in itself, the only parameter affecting the hardness of the material.

Our measurements carried out on experimental materials also demonstrate that there is no linear relationship between the filler content and the initial microhardness. Yet these three materials present the same matrix composition in terms of nature and composition. This means that another factor must be involved. At equivalent volume, the higher the filler content of a material, the greater the proportion of matrix bound to the fillers. This matrix in contact with the fillers probably does not have the same mechanical properties as the matrix resin not in contact with the fillers. A matrix region doubtless exists with optimized mechanical properties ensuring a transition between the hard filler and the softer matrix.[18] The lower the filler content of the material, the less it will present this optimized matrix zone, relatively speaking, helping to explain the absence of a proportional relationship between the filler content and microhardness.

In our study, it is observed that immersion in distilled water at 37°C leads to variations in the microhardness values of the materials tested. Following the long-term immersion of the materials in distilled water at 37°C, two phenomena generating opposite consequences in terms of microhardness are liable to occur. Initially, the water molecules will have a plasticizing effect, inserting themselves between the polymer network chains. The resin matrix will then swell, and the frictional forces between the chains will decrease.[29] Furthermore, tensile stresses are generated at the resin-filler interfaces, straining the bonds in the inorganic component and increasing the frictional forces between filler and matrix resin, facilitating pull out of fillers.[12,30] Conversely, storage of the samples at 37°C can promote new monomer conversions or additional postcuring cross-linking reactions in the resin phase over time.[31-33] In terms of microhardness, these two phenomena have completely opposing consequences, with water promoting a reduction while heat promotes an increase: the variations in values recorded at the different immersion time points are the complex result of various interacting factors. It is essential to note that the postpolymerization induced by the rise in temperature is dependent on the conversion rate initially obtained before immersion and the three-dimensional structure of the polymer network. Indeed, for postpolymerization to occur, there needs to be the possibility of movement for nonsaturated chains. Hence, the higher the initial conversion rate, the less postpolymerization will occur.[34,35] The high initial hardness associated with a high filler content is also a factor that may potentially restrict molecular mobility within the polymer network initially developed.[15] Thus, for example, a marked reduction in microhardness values is clearly observed following one week of immersion for GHF and GRF, whereas that is not the case for XTE or CLI. In addition, in a recent study,[36] the extremely high conversion rate for GRF immediately after photopolymerization was demonstrated, in line with our observations. For the experimental materials, the potential impact of a high filler content on molecular mobility can also be observed in view of the values recorded for EXPA compared with EXPB and EXPC. For these materials with the highest filler content, it can therefore be seen that the effect of water is more dominant than the effect of temperature. It should also be highlighted that, at an equivalent matrix volume, a filled material has been shown to be capable of absorbing more water than an unfilled material due to the capillary penetration routes offered by the silanized interfaces between the fillers and the matrix, which are liable to become hydrolyzed, thus transporting and holding water.[37]

Over time, compared with the values measured after one week of immersion, a relatively steady increase in microhardness is observed for all the materials. For GHF, for which the values were initially significantly reduced after one week of immersion, the potential mobility of the chains and the formation of new bonds are not sufficient to compensate for the effect of the water and restore postpolymerization microhardness values. After two years, the values for GRF and EXPA are close to the initial postpolymerization values. For the materials with a lower filler content—XTE and CLI or EXPB and EXPC—after two years of immersion, the possibility of forming new bonds between the molecular chains has become more important than the effect of water.

To date, no other study has monitored the microhardness of materials over such a long period. For our materials and in our experimental conditions, microhardness values are shown to be maintained, or even increased, after two years compared with initial values, except in the case of GHF, indirectly reflecting preservation of the mechanical properties in the medium term. Obviously, the superimposition and interdependence of the various factors influencing microhardness make interpretation of the results complicated. However, it appears that a very high initial microhardness, combined with a high filler content, is not an adequate guarantee to protect against the detrimental effects of water in terms of plasticization.

It is important to specify that in our protocol, the samples are photopolymerized for a total of 400 seconds, with 200 seconds of light exposure per surface. This method probably optimized the conversion rate compared with the photopolymerization usually performed in clinical situations and restricts the possibilities of postpolymerization.[38] Conversely, the distilled water chosen as the immersion medium here is known to cause polymer structure changes similar to those found with artificial saliva,[39,40] but less marked than with ethanol,[10,15] coffee, or sweetened fizzy drinks, for example.[13,41]

With respect to the rheological properties, it can be noted that, before photopolymerization, all the materials tested in our study are non-Newtonian fluids (ie, they present a nonconstant viscosity that depends on the shear applied). In addition, for all the materials, a reduction in said apparent viscosity is observed, with an increase in the velocity gradient (increase in angular frequency): they therefore present shear-thinning behavior. This can probably be explained by a progressive alignment of the molecules in the thickness of the material under the effect of the shear rate, promoting their relative slip. A second potential explanation is a change in the structure of the material as a result of rupture of the Van der Waals bonds joining nonphotopolymerized monomers. The nature and proportion of the various monomers obviously play an important role in viscosity. BisGMA, with its two hydroxyl radicals per molecule, increases the viscosity of monomer mixtures, promoting the formation of hydrogen bonds between the monomers.[27] Therefore, a mixture of monomers containing BisEMA, a molecule with an identical structure to BisGMA except for the hydroxyl groups that have been substituted, presents a lower viscosity than a mixture of BisGMA.[28] The low density of molecular stacking due to the intrinsic structure of BisGMA and the resulting high free volume also contribute to the higher viscosity of monomer mixtures containing a high proportion of BisGMA.[28] Conversely, TEGDMA, a small molecule with no aromatic cycle or hydroxyl radicals, helps lower the viscosity of monomer mixtures.

Examination of the results obtained for our experimental materials, with equivalent filler and matrix types, indicates the influence of filler contents on rheological behavior: here, the higher the material's filler content, the more viscous it is, irrespective of the shear rate. The results for CLI, with its low filler content in comparison to the other commercially available materials, are also in line with this. However, examination of the results for GRF, GHF, and XTE clearly reveals the impact of other parameters apart from filler content alone, in view of the absence of correlation between the latter and rheological behavior. The type and shape of fillers, along with the quality of silanization, probably have a greater influence here than the filler content itself, which would therefore be consistent with the observations of a recent study.[42] Examination of Figures 1 and 2 shows that, excluding CLI, GRF has the lowest viscosity at all the frequencies and the lowest storage modulus at all the frequencies, with, nonetheless, a steep slope at said low frequencies: these data reflect its excellent spreadability inside small cavities or in pits and fissures, whereas it presents a filler content by mass that is almost 20% higher than that of XTE (data not presented: calculation of the slopes of the curves at low frequencies clearly indicates the steepest slope for GRF). In other words, its low viscosity was not obtained to the detriment of its filler content. GRF therefore offers what appears to be a very interesting compromise between a low viscosity and a low elastic behavior at low shear frequencies and high filler content.

It nonetheless remains true that the spreadability of a material in a small cavity is subject to influences other than viscosity alone: surface tension after etching of dental tissues and the adhesive system used also play a role.[42]

CONCLUSION

For the materials tested, with the limitations related to the experimental conditions and the number of samples prepared, it appears that:

- The filler content values communicated by manufacturers have to be regarded with a certain amount of caution.
- The surface microhardness of materials seems to be affected by numerous interdependent factors, one of the main ones appearing to be the filler content; however, at equivalent filler contents, the polymer structure appears to be important.
- An immersion period of two years in distilled water at 37°C seems to have variable effects on the surface microhardness of the materials; a very high initial microhardness, combined with a high filler content is probably not an adequate guarantee to protect against the detrimental effects of water in terms of plasticization.
- A low viscosity and a low elastic behavior at low shear frequency before photopolymerization can be combined with a high filler content, thereby appearing to offer a satisfactory compromise between the spreadability of the material and its microhardness after photopolymerization.

Conflict of Interest

The authors have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

(Accepted 28 April 2016)

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