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Viscosity and stickiness of dental resin composites at elevated temperatures

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ABSTRACT

Objective. To investigate the influence of pre-heating different classes of dental resin composites on viscosity and stickiness at five different temperatures.

Methods. Six flowable, five conventional packable, and one thermo-viscous bulk-fill resin composites were heated up to 54 °C in a plate-plate rheometer to determine their complex viscosity. Normal force measurements were carried out for the six packable materials to determine the unplugging force and unplugging work (stickiness) over the same temperature range. Data were analyzed using Kolmogorov–Smirnoff test, one-way ANOVA and Tukey Post Hoc test with $\alpha = 0.05$ as level of significance.

Results. At 23 °C packable composites showed viscosity between 6.75 and 19.14 kPa s, while flowable composites presented significantly lower viscosities between 1.31 and 2.20 kPa s. Pre-heating led to a drop of 30–82% in the viscosity of packable materials. The thermo-viscous material dropped to the level of flowables at 45 and 54 °C thus behaving as a packable composite at room temperature with flowable-like viscosity at higher temperatures. No statistically significant differences for viscosity were observed among flowable composites at any temperature.

The unplugging force decreased for packable composites, while their unplugging work generally increased at elevated temperature. At 23 °C unplugging force was measured between 7.50 and 19.18 N, while pre-heating up to 54 °C led to values between 2.9 and 6.2 N. Regarding unplugging work at 23 °C the calculated values were between 3.0 and 8.9×10^{-3} J and at 54 °C between 8.8 and 13.0×10^{-3} J.

Significance. Pre-heating significantly reduced viscosity of highly viscous resin composites, while no influence was shown for flowable composites. In general stickiness, measured as unplugging work, increased at elevated temperatures. The thermo-viscous material showed low viscosity comparable to flowable composites at 45 and 54 °C, yet its stickiness did not increase significantly compared to the values at 23 °C.

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1. Introduction

Depending on the shape of the cavity for direct resin composite filling therapy, it can be challenging to manage a complete sealing of the tooth substrate and to create an interface to the resin composite without gap formation [1]. Secondary carries is highly associated with the restoration's margins and possibly connected with the gaps between tooth structure and restoration [2], termed microleakage [3]. To improve adaptation, flowable composites can be used as cavity liners [4]. Low viscosity materials are able to increase the wetting effect to the cavity wall, improving marginal adaptation and reducing microleakage [1]. Viscosity is highly dependent on the composition of the resin matrix, filler fraction, filler size distribution and silane treatment of the fillers, as well as the interaction between fillers and the matrix [5,6]. However, those differences in composition are also reflected by inferior material properties as flowables are known to exhibit reduced flexural strength or elastic modulus compared with their packable counterparts [7–9].

A practical approach to improve adaptation is to lower the viscosity of packable resin composites during application without compromising their mechanical properties. Resin composites behave as non-Newtonian viscoelastic fluids, showing shear thinning behavior [10]. As viscosity decreases under shear loading, resin composites become more fluid during adaptation to the tooth structure [11]. A significant reduction of viscosity can also be achieved by pre-heating packable composites before application [10]. At elevated temperatures, thermal vibrations force monomers of the matrix further apart and allow them to slide by each other more easily which lowers the internal friction [1]. The influence of temperature on viscosity is explained by the Arrhenius equation ($\eta = A * e^{-E/RT}$; η: temperature dependent complex viscosity; A: proportional coefficient; E: activation energy for flow; R: gas coefficient; T: temperature), which describes the correlation between fluid viscosity and temperature [12]. Plotting the logarithm of η against the reciprocal temperature ($1/T$) results in a linear behavior for materials that follow the Arrhenius law [13].

A new thermo-viscous bulk fill material has been developed accordingly, which allows pre-heating up to 65 °C (dispenser) or even to 68 °C (caps warmer) before application [14]. New monomer chemistries that may require heat resistant initiator systems become a challenge in this type of material [15]. Whether a thermo-viscous resin composite can reach viscosity levels compared to that of flowable materials yet managing to maintain clinical acceptable handling properties in its pre-heated state, has not been fully elucidated in previous studies.

Stickiness, in context of a clinical scenario, is the ability of a resin based restorative or luting composite to adhere and stick to the surface of a dental placement instrument. For a dentist, this is a critical handling property, which may cause the 'pull out' of material from a cavity, in turn affecting form, shape and marginal integrity of restorations [16]. Composites should not stick to the plunger while filling the cavity, because porosities and voids are more likely to be formed [17]. A relation has been found between open margins and highly sticky materials [18]. On the molecular level, the adhesion between a placement instrument and the restorative material is established via comparably weak dipole (van der Walls) interactions [19]. Furthermore, wettability and unplugging force or work are expected to correlate with paste viscosity, in terms of reduced wetting at higher viscosities and reduced resistance to detachment. This is supported by the fact that interfacial interactions between fillers and monomers have an impact on viscoelastic properties of resin composites and in turn on their stickiness [20]. Identifying the maximum unplugging force at detachment or the unplugging work (defined as the integrated area of force and displacement), are measurements previously employed to determine stickiness in the laboratory [21]. Different settings were designed to provide reproducible results. Some studies lowered a flat-ended stainless steel probe or instrument into a resin composite portion [15,16,22], others noted individual qualitative assessment by dental practitioners that give a scale of composite stickiness as a description of handling behavior [23]. To our knowledge, there is no previous work that has assessed the stickiness of dental resin composites with the use of a plate-plate rheometer. Reducing resin composite viscosity by pre-heating may improve wettability and result in higher energy for separation from the instrument [24]. Thereby, changes in temperature have an influence on unplugging force, unplugging work reveals variations in molecular linkages that relate to the shear behavior [15].

Consequently, the aim of this study was to investigate the influence of temperature on the viscosity and stickiness of uncured packable and flowable resin composites, and how they compare to a new thermo-viscous bulk fill composite. We hypothesize that pre-heating is reducing viscosity of packable and flowable resin composites, and that a temperature increase will negatively affect stickiness of packable resin composites (unplugging force and unplugging work).

2. Materials and methods

The influence of pre-heating on viscosity and stickiness was investigated for six flowable, five packable, and one thermo-viscous bulk fill resin composites. Material composition, specifications and abbreviations are listed in Table 1. Viscosity measurements were performed for all materials while stickiness was tested only for the packable and the thermo-viscous materials.

2.1. Viscosity

Viscosity is defined as the extension of internal friction in a fluid and is measured as force per unit area resisting uniform flow. Resin composites are non-Newtonian fluids showing viscoelastic behavior. This can be characterized by oscillating shear deformation tests in a rheometer. Thereby the contribution of the elastic part is described by the storage modulus G', that of the viscous part by the loss modulus G''. $\tan\delta$ is the ratio of loss to the storage modulus. The complex shear modulus (G^*) uses the imaginary loss modulus (iG'') and is given by Eq. (1):

$$G* = G' + iG'' \quad (1)$$

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Table 1 – Materials under investigation ordered alphabetically (abbreviation codes), manufacturer, classification, batch number and monomer and filler compositions as published by manufacturers.

Material (code)	Manufacturer	Classification	Batch-nr.	Matrix	Fillers
CLEARFIL MAJESTY™ Flow (CMF)	Kuraray Noritake	Posterior region nano-hybrid flowable	B20052	TEGDMA Hydrophobic aromatic dimethacrylate	81 wt%/62 vol% -silanated barium glass fillers (average 3 μm) -silanated colloidal silica (average 20 nm)
CLEARFIL MAJESTY™ Posterior (CMP)	Kuraray Noritake	Posterior region nano-hybrid packable	7L0064	BIS-GMA TEGDMA Hydrophobic aromatic dimethacrylate	92 wt%/82 vol% -silanated glass ceramic fillers (average 1.5 μm) -surface treated alumina micro fillers (average 20 nm) -silanated silica filler
Ecosite Elements HIGHLIGHTS (EEH)	DMG	Universal nano-hybrid flowable	803736	EBPADMA BIS-GMA TEDMA	65 wt%/38 vol%(0.02 –0.7 μm) -Ba glass
Ecosite Elements PURE (EEP)	DMG	Universal nano-hybrid packable	803725	EBPADMA BIS-GMA	81 wt%/65 vol%(0.02 –0.7 μm) -Ba glass
Filtek™ Supreme XTE (FSX)	3M™	Universal nano-hybrid packable	NA01835	BIS-GMA UDMA TEGDMA BIS-EMA PEGDMA	78.5 wt%/63.3 vol% -silica fillers (20 nm) -zirconia fillers (4–11 nm) -zirconia-silica-cluster (0.6–20 μm)
Filtek™ Supreme XTE Flowable (FSF)	3M™	Universal nano-hybrid flowable	N998213	BIS-EMA BIS-GMA EBADMA	65 wt%/55 vol% silica-fillers <5% YbF_3
Grandio®SO (GSO)	VOCO	Universal nano-hybrid packable	1851244	BIS-GMA TEGDMA BIS-EMA	89 wt%/73 vol% inorganic fillers -glass ceramic fillers (average particle size 1 μm) -functionalized siliciumdioxide nano particles (size 20–40 nm)
Grandio®SO Flow (GSF)	VOCO	Universal nano-hybrid flowable	1912388	HEDMA BIS-GMA TEGDMA BIS-EMA	81 wt%/65 vol% inorganic fillers -glass ceramic fillers (average particle size 1 μm) -functionalized siliciumdioxide nano particles (size 20–40 nm)
Grandio®SO Light Flow (GSL)	VOCO	Nano-hybrid highly flowable	V76859	BIS-GMA BIS-EMA TEGDMA Aliphatic dimethacrylate 1,6-Hexa-nediylbis-methacrylate	76% wt inorganic fillers
Venus® Diamond Flow (VDF)	Kulzer	Universal nano-hybrid flowable	K010213	UDMA EBADMA TEGDMA	65 wt%/41 vol% (0.02–5 μm) -Ba-Al-F silicate glass -10–25% YbF_3 -SiO_2
Venus® Pearl (VPE)	Kulzer	Universal nano-hybrid packable	K010054	TCD-Urethane-acrylate UDMA TEGDMA Polymer	59 vol% (particle size 5 nm-5 μm) -Barium aluminum boro fluor silicate glass -Silica
VisCalor® bulk (VCB)	VOCO	Thermo-viscous bulk fill	V76291	BIS-GMA Aliphatic dimethacrylate	83 wt% inorganic fillers

The complex viscosity (η^*) is calculated (Eq. (2)) upon the ratio of the complex shear modulus and the frequency of oscillation (ω):

$$\eta* = G* / \omega \quad (2)$$

An empirical relation (Cox-Merz) often relates both types of viscosity [25–27]. According to Cox-Merz, steady-state shear and complex viscosities are equal when the shear strain applied on the polymer is equal to the frequency of oscillation (ω) employed for testing the same polymer through oscillatory tests.

Viscosity measurements on the resin composites were performed using a rheometer (Physica MCR 301, Anton Paar, Graz, Austria) equipped with an aluminum plate-plate configuration in a temperature-controlled test chamber (Peltier,

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H-PTD200). The rheological properties of a viscoelastic material are independent of strain up to a critical strain level (linear viscoelastic region). A preliminary test was performed in order to measure the limit of the linear viscoelastic region (LVE region) and to choose the right range of amplitude for the next tests, without destroying the structure of the samples. A strain rate of 0.1–100% and a frequency of 1 Hz were used at five different temperatures (23, 30, 37, 45 and 54 °C) for each material (dynamic strain sweep). The results appear as a diagram with strain plotted on the x-axis and storage modulus G' and loss modulus G'' plotted on the y-axis (Controlled Shear Deformation Graph). LVE region is calculated by analysis software.

Complex viscosity of all twelve resin composites (packables and flowables) were tested in oscillation using a parallel plate geometry with a 25 mm radius. The gap between the plates was set to 0.25 mm for all materials. Any excess of resin composite material or air bubbles arising around the circumference of the plate were manually removed prior to initiating the measurements. Testing was performed ($n = 10$ per material) at five different temperatures (23, 30, 37, 45 and 54 °C).

2.2. Stickiness

Stickiness can be quantified by vertical detachment tests determining unplugging force or unplugging work. Testing was performed for the six packable materials with the same rheometer as used for viscosity measurements, but adjusted as follows: The upper 8 mm aluminum plate was covered with a stainless-steel surface and polished up to 4000 grit (0.1 μm roughness) to imitate the stainless-steel instruments dentists use in clinical practice. The rheometer was equipped with a load cell (50 N; accuracy ± 0.03 N) for measurement of normal forces to the plate.

The resin composite samples were placed in a gap of 1 mm between the plates which was automatically adjusted prior to each measurement to ensure applied force was zero at the beginning. Any excess material was removed before testing. The tensile loading rate for the pull-off test was 5 mm/s, which fits within the range used in previous studies [15,16,28]. The unplugging force was measured until the upper plate and the resin composite were detached and the maximum value was recorded. As flowable materials would stick to both upper and lower plates, no separation force could be measured, and the reason why only the packable materials were tested in stickiness measurements. Based on the force-displacement graph, the work needed for separation (unplugging work) was calculated from the area under the curve. In case the resin composite was separated from the bottom plate and moved upwards with the upper plate, the measurement was considered invalid. All tests were performed for each temperature (23, 30, 37, 45, 54 °C) and material ($n = 10$ per material).

2.3. Statistical analysis

Data were analyzed using statistical software (SPSS Statistics 21, IBM, Chicago, USA). Kolmogorov–Smirnov test was applied to check for a normal, Gaussian distribution. One-Way ANOVA and Student–Newman–Keuls Post Hoc test served to analyze the statistical differences at a level of significance of $\alpha = 0.05$.

3. Results

3.1. Complex viscosity

Mean values for complex viscosity for each material at five different temperatures (23, 30, 37, 45, 54 °C) with standard deviations are shown in Table 2 and depicted in Fig. 1. The results for complex viscosity were evaluated for following Arrhenius' law. This can be valued by plotting the logarithm of the complex viscosity η against the reciprocal temperature ($1/T$). Fig. 1 shows, that all materials showed a mostly linear behavior over the tested temperatures in the graph. Activation energies "E", calculated following Arrhenius' equation ($\underline{\eta} = A * e^{-E/RT}$, η: temperature dependent complex viscosity; A: proportional coefficient; R: gas coefficient; T: temperature) according to the trend lines' gradients are shown in Table 2.

Among packable materials complex viscosity generally decreased with increasing temperature. For all materials there was a significant difference between 23 and 54 °C. At 23 °C VPE showed the significantly highest and EEP the significantly lowest complex viscosity. CMP showed the significantly highest and VCB the significantly lowest complex viscosity at 54 °C. Between 30 and 37 °C there was a statistically significant difference for all materials except for EEP and CMP. Also, between 37 and 45 °C there was a statistically significant difference for all materials except for EEP, CMP and VCB. No further significant drop was observed for any material between 45 and 54 °C except for FSX. CMP showed the smallest reduction (30%) in complex viscosity from 23 to 54 °C. The complex viscosity of VCB decreased the most (82%) in the same temperature range.

Concerning complex viscosity of the flowable composite materials, no statistically significant differences were observed between different temperatures for any material. At 23 °C the complex viscosity of the flowables was lower in a range of 206.8–1361% compared to the packable ones, while at 54 °C it was lower in a range of 130–434%. The thermo-viscous bulk fill material VCB showed a decrease in mean complex viscosity values from 11.59 kPa s at 23 °C to 2.06 kPa s at 54 °C, hence reaching the complex viscosity range of flowable composites already at a temperature of 45 °C.

3.2. Stickiness

Unplugging force and unplugging work were measured to describe the stickiness of the packable resin composites to placement instruments. The influence of temperature on these two parameters is shown in Fig. 2 for unplugging force and in Fig. 3 for unplugging work. The mean values and standard deviations are listed in Tables 3 and 4, respectively.

Stickiness measurements of the packable resin composites showed a decreasing unplugging force with temperature. Contrary, unplugging work generally increased at elevated temperatures. At 23 °C VCB had the highest and CMP the significantly lowest value of unplugging force. At 54 °C FSX had the highest and GSO the lowest unplugging force, but the differences were not significant. VCB presented the highest reduction of unplugging force between 23 and 54 °C (82%) and CMP the lowest (34%). For unplugging work VCB had the significantly highest and CMP the lowest value at 23 °C. At 54 °C

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Table 2 – Mean values for complex viscosity η^* [kPa s] for each material at five different temperatures (23, 30, 37, 45, 54 °C) with standard deviations in brackets; activation energy calculated following Arrhenius' equation ($\eta = A * e^{-E/RT}$) according to the trend lines' gradients.

Material	Complex viscosity, η^* [kPa s]					Activation energy, E [kJ mol^{-1}]
	23 °C	30 °C	37 °C	45 °C	54 °C	
CMF	1.64(0.05)	1.65(0.03)	1.65(0.04)	1.69(0.04)	1.69(0.05)	0.90
CMP	10.46(0.13)	9.36(0.11)	8.55(0.06)	7.71(0.08)	7.00(0.15)	10.39
EEH	1.75(0.07)	1.60(0.05)	1.48(0.05)	1.39(0.08)	1.36(0.10)	6.71
EEP	6.75(0.60)	5.50(0.53)	4.71(0.35)	4.16(0.19)	3.89(0.11)	14.37
FSX	16.81(0.56)	11.01(0.38)	8.31(0.27)	6.09(0.19)	4.83(0.17)	32.20
FSF	1.31(0.04)	1.31(0.03)	1.32(0.03)	1.34(0.02)	1.33(0.03)	0.55
GSO	8.99(0.72)	7.14(0.82)	5.30(0.69)	4.02(0.83)	3.68(0.23)	24.55
GSF	2.20(0.09)	2.16(0.08)	2.11(0.06)	2.06(0.05)	2.04(0.04)	2.04
GSL	1.55(0.15)	1.50(0.14)	1.48(0.15)	1.48(0.15)	1.48(0.14)	1.22
VDF	1.79(0.04)	1.65(0.07)	1.55(0.07)	1.42(0.08)	1.37(0.06)	7.13
VPE	19.14(3.13)	12.25(1.67)	7.80(1.48)	5.12(0.74)	4.70(0.51)	38.25
VCB	11.59(0.56)	4.98(0.46)	2.93(0.17)	2.34(0.44)	2.06(0.37)	43.65

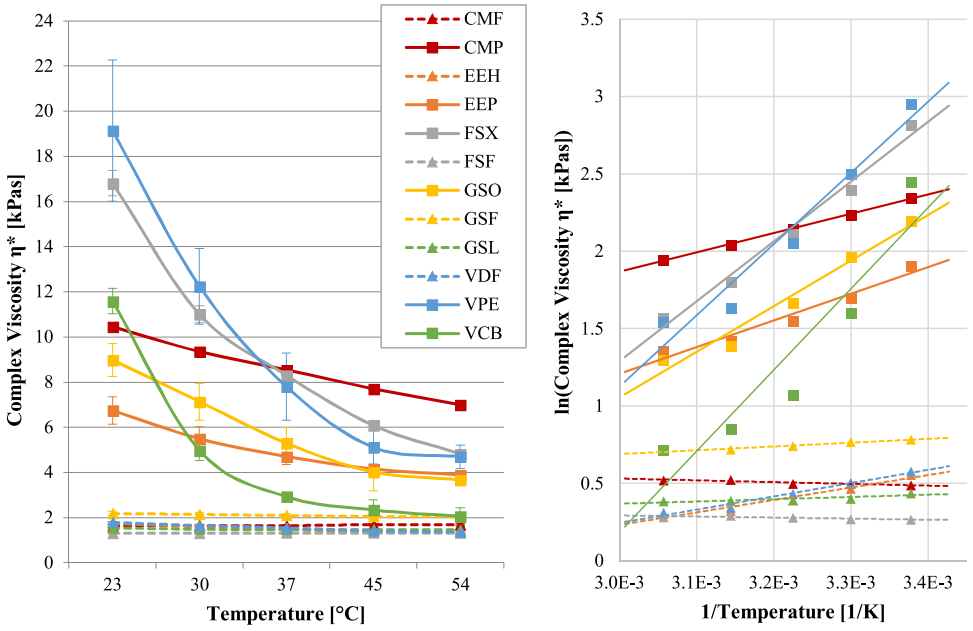

Fig. 1 – Left side: Development of complex viscosity (η) [kPa s] of flowable (triangles) and packable (squares) resin composite materials with increasing temperature (mean values ± standard deviations); Right side: natural logarithm of the complex viscosity (η) values [kPa s] (y-axis) against the reciprocal temperature (1/T) [1/K] (x-axis). Trendlines for flowable (dotted) and packable (continuous) materials indicate a linear behavior following Arrhenius' law.

Table 3 – Mean values for maximum unplugging force F_{max} [N] for each material tested at five different temperatures (23, 30, 37, 45, 54 °C) with standard deviations in brackets.

Material	Maximum unplugging force, F_{max} [N]				
	23 °C	30 °C	37 °C	45 °C	54 °C
CMP	7.50(0.45)	7.03(0.91)	6.60(0.58)	5.64(1.25)	4.88(0.64)
EEP	14.76(1.31)	11.45(1.97)	9.94(0.53)	7.19(0.79)	5.31(0.22)
FSX	17.74(1.14)	10.35(1.62)	9.10(0.35)	7.14(0.55)	6.19(0.35)
GSO	8.39(0.44)	6.51(0.69)	5.14(0.43)	3.80(0.36)	2.93(0.34)
VPE	10.67(1.00)	7.29(0.91)	4.35(0.30)	3.65(0.36)	3.33(0.34)
VCB	19.18(3.21)	13.48(1.71)	10.33(0.60)	6.72(0.19)	3.19(0.17)

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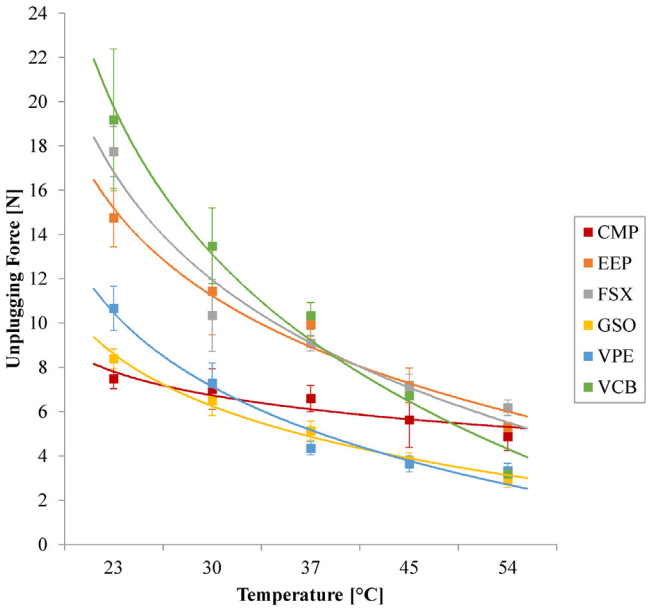

Fig. 2 – Unplugging force [N] with increasing temperature (23, 30, 37, 45, 54 °C) for each material (mean values ± standard deviations).

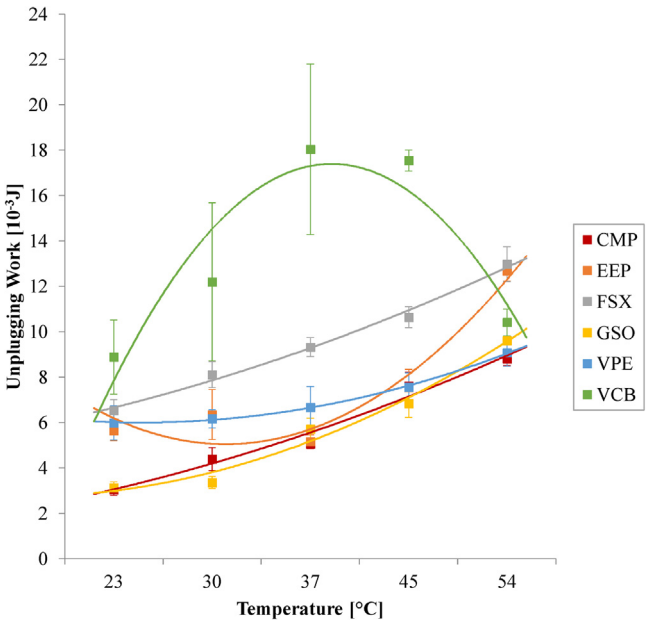

Fig. 3 – Unplugging work [10^{-3} J] with increasing temperature (23, 30, 37, 45, 54 °C) for each material (mean values ± standard deviations).

FSX had the highest and CMP the lowest value, but not in a significant way. At 37 °C VCB presented the highest value of unplugging work among all temperatures and materials. Between 23 and 54 °C, GSO had the highest (207%) and VCB the lowest (15%) increase concerning unplugging work. No statistically significant difference could be found for the unplugging work of VCB at 23 and 54 °C.

4. Discussion

4.1. *Viscosity*

According to our results, a significant decrease in complex viscosity at elevated temperatures was only observed for the packable, but not for the flowable resin composites. Packable resin composites were more sensitive to temperature increase, especially between 23 and 37 °C (Fig. 1). These findings cannot be only explained by the filler packing only, since some flowables have as much or more fillers than some packables. Filler loadings of the flowable materials tested vary between 38 vol% (EEP) and 65 vol% (GSF), those of the packable materials are listed from 59 vol% (VPE) to 82 vol% (CMP) as shown in Table 1. Lee at al. [12] stated that viscosity of resin composites can vary significantly even among those of the same class. The high filler load of the flowable GSO is thereby only achievable by using high fractions of nano-fillers. Viscoelastic properties are not only related to filler content, but also highly influenced by filler-matrix interaction and interlocking [20]. Since the inorganic ceramic fillers are negligibly affected at pre-heating temperature ranges [29], interfacial interactions depend highly on the hydrodynamic force working at the particle surface [10]. This interaction theory could explain the findings of the present study, where a higher complex viscosity of VPE was recorded compared with CMP at 23 °C (19.14 vs. 10.46 kPa s, respectively). The functionalized siliciumdioxide nano particles in CMP might result in a higher flowability despite the substantially lower filler loading of VPE. Furthermore, the ranking of these two materials swaps at 45° and 54°, highlighting that not only the amount of fillers is determining viscosity, but interactions between resin matrix and fillers may vary in extend or even change at different temperatures. Elbishari et al. [6] suggested that viscosity increases

Table 4 – Mean values for unplugging work [10^{-3} J] for each material tested at five different temperatures (23, 30, 37, 45, 54 °C) with standard deviations in brackets.

Material	Total unplugging work [10^{-3} J]				
	23 °C	30 °C	37 °C	45 °C	54 °C
CMP	3.04(0.26)	4.39(0.51)	5.07(0.21)	7.62(0.61)	8.81(0.30)
EEP	5.64(0.44)	6.35(1.11)	5.18(0.28)	7.55(0.79)	12.67(0.45)
FSX	6.53(0.48)	8.11(0.57)	9.33(0.42)	10.64(0.46)	12.99(0.77)
GSO	3.13(0.26)	3.36(0.27)	5.71(0.49)	6.85(0.62)	9.62(0.64)
VPE	5.99(0.76)	6.17(0.40)	6.67(0.92)	7.57(0.62)	9.08(0.59)
VCB	8.89(1.64)	12.20(3.47)	18.04(3.76)	17.55(0.46)	10.41(0.59)

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with larger filler sizes, and at different temperatures (23 or 37 °C), providing further evidence for the increased complex viscosity of VPE (5 μm average filler diameter) compared with CMP (1.5 μm). Those findings may also explain the high filler content (65 vol%) and small average filler size (1 μm diameter) of GSF whilst still exhibiting non-significant differences in complex viscosity compared with the other flowable materials investigated here.

In the present study a plate to plate geometry rheometer with 25 mm upper plate and 0.25 mm gap was used to measure complex viscosity of the composites at different temperatures. Different parameters such as gap, plate diameter, amplitude and frequency can have a significant impact on viscosity resin composite materials. Lee et al. [25] used a cone to plate geometry rheometer with a cone angle of 0.1 radius to show the influence of increasing frequency (shear rate) on complex viscosity. In another study Lee et al. [30] used an upper plate of 20 mm diameter and a gap of 1 mm in order to measure viscosity of flowable composites which is similar to the tall plate used in the current investigation. Ahn et al. [31] used a plate to plate geometry with 8 mm upper plate and a gap of 1 mm and showed the influence of temperature increase and strain rate on shear storage modulus G' and complex viscosity η^*. The material they tested (Filtek Z350, 3M) has a comparable composition to FSX. Due to the preliminar determination of the LVE-region, a strain rate of 0.2% was employed for FSX. In the study of Ahn et al. [31], strains above 0.1% showed lower G' and η^* values for the pre-heated (60 °C) material compared with room temperature (25 °C) measurements, which agrees with the current findings. Al-Ahdal et al. [10] measured viscosity in a rheometer at 23 and 37 °C. For flowable composites, viscosity significantly decreased with increasing temperature. Although the authors measured only nominal change in values for flowable composites, which was comparable to the current findings, their initial values at 23 °C were smaller for VDF (0.12 ± 0.02 vs. 1.79 ± 0.04 kPa s). Regarding packable resin composites viscosity was much higher at 23 °C for FSX (349.33 ± 13.8 vs. 16.81 ± 0.56 kPa s) and VPE (104.2 ± 0.72 vs. 19.14 ± 3.13 kPa s), possibly due to a different experimental set-up and their calculation of the mean values over a varying shear rate range. At 37 °C the viscosity for VPE (13.14 ± 2.87 kPas) was comparable to our measurements (12.25 ± 1.67 kPas). Dionysopoulos et al. [32] measured the reduction of viscosity after pre-heating by determining film thicknesses. Despite the different methodology they found a reduction of 25% between 23and 54 °C for CMP, which roughly corresponds to our result of 33% decrease.

The activation energies for flow calculated by Arrhenius' equation are shown in Table 2. Although all materials show linear regressions (Fig. 1) and seem to follow Arrhenius' law, the activation energies indicate, that temperature in the observed range between 23 and 54 °C does not have an influence on flowable resin composite viscosity. In flowable resin composites, the amount of reinforcing fillers as well as the size of the filler particles does not exceed percolation in the resin network so that internal friction is not yet temperature dependent. The values for activation energies of the packable resin composites are comparable to other authors [33,34]. Alnazzawi examined two identical and one comparable material, finding activation energies in the same dimensions to the present study ([present study/reference] GSO: 24.55/42.21 kJ mol^{-1}, FSX: 32.20/41.48 kJ mol^{-1}, VPE/Venus Diamond Flow: 38.25/48.77 kJ mol^{-1}) [35]. In the present investigation VCB showed the highest activation energy (43.65 kJ mol^{-1}). Certainly, a single comparison of activation energies does not hold for the differences in complex viscosity as condensable materials under investigation are of varying resin monomer composition and varying filler configuration (see Table 1). Increasing the processing temperature from 23 to 54 °C, condensable resin composites are reaching the viscosity of their flowable counterparts and in consequence are offering improved adaptation in an oral cavity.

4.2. *Stickiness*

Unplugging work as a predictor for stickiness increased generally for all packable materials by pre-heating. Viscosity, filler volume and monomer matrix composition can have an influence on the stickiness of materials [12]. Ertl et al. detected that materials with reduced filler loading, consequently resulting in a greater fraction of resin matrix, showed higher stickiness due to their formulation [16]. This finding is in accordance with the present results, where FSX (63.3 vol% filler load) showed higher unplugging work at each temperature tested compared to GSO and CMP (73 and 82 vol% filler load). Furthermore, not only the amount but also the composition of the resin matrix has an influence on stickiness. Monomers containing functional groups with dipole character (like Bis-GMA) are responsible for the composite's polarity and might thereby trigger a sticky behavior to polar surfaces like metal instruments [16,21]. According to the manufacturer, CMP contains strongly hydrophobic matrix monomers. Originally designed for reducing the water sorption of the cured resin composite, these monomers might as well be a reason for CMP showing the lowest unplugging work at 23, 37 and 54° C in the present study.

For stickiness testing the same rheometer was used as for complex viscosity measurements. This set-up is reliable with low technique sensitivity and a reproducible method, showing low variance. By adjusting the upper plate with a stainless-steel surface instead of aluminum, simulation of the clinical situation was improved. Stickiness has been previously studied by indirectly analyzing unplugging force and work by curing and measuring the height and shape of sticky composites following elevation with a flat-ended stainless steel instrument [36]. In that study, maximum peak height and area generally increased with temperature and was affected by filler morphology of the composites. Using an adapted method by the same research group, Kaleem et al. [28] investigated an inverted trend to our measurements, where unplugging force increased with higher temperatures. On the one hand, they performed testing only up to 37 °C, by heating a thermostatically controlled mold, not working in a high temperature environment. Furthermore, it cannot be determined if this trend evolved for higher temperatures as well. On the other hand, the increased contact surface area due to different set-ups (a probe dipping into the uncured material in a cavity-like form instead of a plate-to-plate geometry) most probably account for the observed differences. Those

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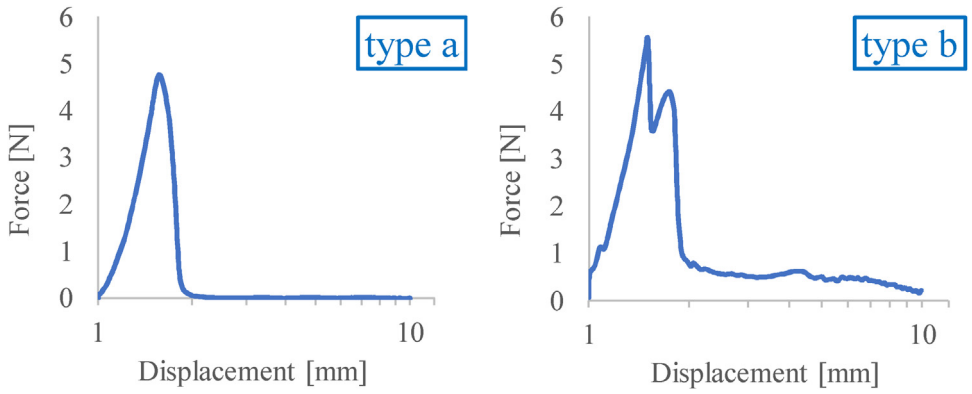

Fig. 4 – Type a (left) of force-displacement curves with a singular maximum (using the example of one VCB specimen at 37 °C) and type b (right) showing a secondary maximum described by unplugging force (*y*-axis) and displacement (*x*-axis) during stickiness testing.

differences should have been smaller though, rather than a complete inverse switch in trend. Maybe the plate-to-plate geometry may include a confounding (or over-riding) effect of material viscoelasticity with temperature. Furthermore, the curve profiles are influenced by a combination of stress-strain-behavior of the resin composite itself and of the interfacial interactions between probe surface and uncured material [21]. Added to that, roughness of the plate or probe and included air bubbles in the contact area might play a role [37]. Rosentritt et al. showed a good relationship between laboratory and clinical evaluation by combining clinical experience of dentists with laboratory testing methods [22,23]. Similar to the present investigation, those authors showed a general increase of unplugging work with increasing temperature. Their results for GSO, as the only identically tested material, were in the same range at 25 °C (compared to our 23 °C) and 37 °C.

Noteworthy, two typical types of force-displacement behavior were observed during testing. Fig. 4 shows the most frequent type "a" with a single peak, and the less common type "b" with two peaks, or with a secondary maximum/shoulder.

A visible secondary maximum represents the stretchiness of the material. Here, the separation between the resin composite and the plate is more gradual. If bonding forces between the resin composite and the plate are lower than the force needed for stretching the material, the secondary maximum will be lower or even absent. After the single peak, the force decreases instantaneously and gradually falls to zero. These observations are in agreement with Kaleem et al. [21,28].

Generally, stickiness measurements of the packable resin composites showed a decreasing unplugging force with temperature (apart from VCB). Contrary, unplugging work generally increased at elevated temperatures. The different trend of those results is described in Fig. 5, where two measurements of the same material at 23 and 54 °C are shown. At 23 °C maximum unplugging force is higher than at 54 °C, but the area under the curve (unplugging work) is larger for the measurement at 54 °C. At 54 °C the upper plate is in contact with the material for a longer time and distance during the upward movement. The resin composite in turn stretches more and is

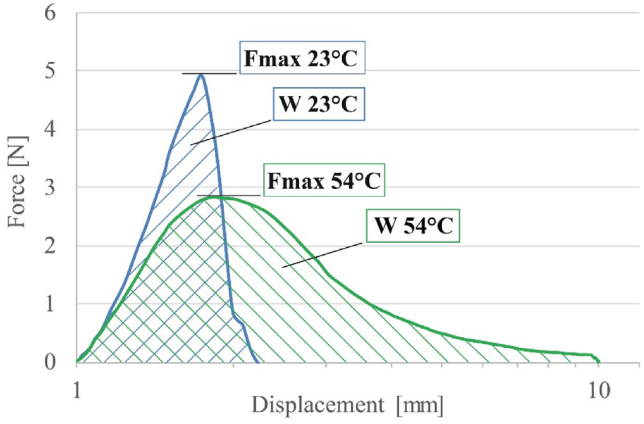

Fig. 5 – Schematic depiction of force-displacement diagrams of the same material at two different temperatures (23/54 °C) showing the differences between maximum unplugging force (peak) and unplugging work (area).

stickier, regardless of the maximum force needed for separation.

Generally, unplugging work is regarded as a more reliable way of measuring stickiness, as it is calculated by the integrated area of force and distance [21]. Yang et al. also stated that unplugging work is more sensitive to changes in elongation than unplugging force and possibly more suitable to characterize stickiness [15]. Furthermore, forces in the range of about 5 N are unlikely to be of significant detriment to clinical handling, and therefore, the work is more predictive of handling properties.

4.3. *Behavior of the thermo-viscous bulk fill material*

VCB presented the highest complex viscosity decrease from 23 to 54 °C (82%) and showed mean values similar to the flowables under investigation at 45 and 54 °C unlike the other packable materials tested. Blalock et al. [29] confirmed that

conventional packable resin composites increased their flowability at higher temperatures but did not reach as small film thicknesses compared with those of flowable resin composites. VCB was the only material that showed no significant difference in unplugging work between 23 and 54 °C having the highest unplugging work among all materials at 37 °C. Yang et al. [15] also reported an increase of unplugging work of VCB by elevating temperature from 22 °C (according to our 23 °C) to 37 °C. Although their absolute values for unplugging work were lower, they measured an increase of 148% after pre-heating for three minutes, which is comparable to our results (103% increase). As the composition of commercial materials are usually proprietary and unknown to the research community, the underlying rheological mechanisms for materials such as VCB remain speculative. In principle one would think of a packable material with high filler load and respective physical properties at room temperature but in turn a flowable, low viscous and easy adaptable material at elevated temperatures. A high filler load accounts for a high amount of internal friction during adaptation. Therefore, filler shape, size and potentially silanization may have been adapted to decrease the internal friction. Another variable might be the underlying monomer chemistry. Viscosity of the resin components will increase with higher molecular weight monomers, longer branching chains and larger potential for hydrogen bonding [38]. The more energy needed to overcome those entanglements, the higher temperature would be required to reach more freely moving monomers and result in decreased viscosity [29]. Shorter and aliphatic monomers might allow better flow properties and apolar monomers might reduce the adhesive stickiness to surfaces, especially at elevated temperatures where the surface wetting might increase.

Fig. 4 (left side) shows the unplugging work for VCB with a peak at 37 °C. The observed parabolic behavior with temperature, where an increase from room to oral temperature resulted in higher unplugging work which decreased at higher temperatures, is difficult to explain without deeper knowledge of the material chemistry. Conventional monomer technology might account for the initial increase in unplugging work, and then novel chemistries only become effective at elevated temperatures. There might be an optimum temperature to use VCB in clinical practice. At 37 °C (i.e. open mouth temperature), the material would exhibit increased stickiness and therefore should be used in a pre-heated state for application. As the temperature decreases following placement (back to 37 °C), the increase in stickiness may aid adaptation to the cavity walls. The material is marketed and applied at even higher temperatures (than our testing at 54 °C) of up to 68 °C, and according to the trend in Fig. 3 one would expect even further reduction in stickiness. Unfortunately, the practical settings in the current study did not allow manual handling at 68 °C and besides, materials pre-heated to such high temperatures may increase the potential detrimental effect on pulp vitality [39]. Substantial temperature increases via resin composite heating that may elicit pulpal reactions in deep cavities also may also be questioned [40,41]. A rise of intrapulpal temperature was measured after placing pre-heated composites, which was amplified by polymerization exotherm and heat from the light curing unit [42–44]. A temperature increase higher than 5.5 °C of the pulpal tissue will cause irreversible damage because of initiated coagulation processes [42].

5. Conclusions

Within the limitations of this study, it can be concluded that pre-heating has an influence on complex viscosity of packable, but not significantly on that of flowable resin composites. Furthermore, the use of rheometer for measuring unplugging force and unplugging work can be used as a practical way of measuring stickiness in a temperature-controlled environment. With elevated temperature unplugging force decreases and unplugging work generally increases. Unplugging work is a more clinically relevant way of measuring stickiness. Within the limitations of this study the thermo-viscous bulk fill material showed a complex viscosity comparable to flowable composites at 54 °C whilst keeping clinically acceptable handling properties.

Conflict of interest

None declared.

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