Rheological approach for determining yield stresses in flowable resin composites prior to setting

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The purpose of this study is to develop a method for quantifying the fluidity of flowable resin composites using determinations of yield stress. Five commercially available composites (AliteFlo LV, Flow-it ALC, Venus flow, Tetric N-flow, Revolution Formula2) were investigated. Yield stress values were obtained by plotting shear stresses for a range of shear rates, followed by fitting of Casson fluid models to flow curve data and extrapolation to the stress axis. To confirm that yield stress reflected fluidity, apparent viscosity at the lower shear rate (0.2 s^{-1}) was calculated from flow curves. Yield stresses ranged from 5.4 to 43.1 Pa, and were found to capture differences in the fluidity of composites that were not captured by viscosity measurement at the low shear rate. Yield stress is directly proportional to fluidity, and could serve as a simple and precise indicator for selecting flowable resin composites for use in various clinical applications.

Keywords: Flowable resin composites, Yield stress, Rheology, Handling characteristics

INTRODUCTION

Selection of flowable resin composites with handling properties that are appropriate for specific clinical situations is an important factor in successful dental restoration. For placement of these materials, flow properties are particularly important. Flowable resin composites have a wide range of clinical applications, including use as pit and fissure sealants and restoration liners and in Class IV and V restorations, and accordingly have widely varying flow properties¹. However, because no standard test method for evaluating the flow properties of these materials has been described, products often lack absolute assessments. Instead, manufacturers only report comparisons of flow distances of resin composites on a vertical plane. Previous studies report flow properties of flowable resin composites using various methods, including the flow test specified in ADA and ISO standards^{2,3} with modification⁴⁻⁶, measurements of aspect ratios of slumped composites after extrusion⁷, and rheometer-based measurements of dynamic flow properties⁸⁻¹³. Among these methods, dynamic rheological measurements are the most accurate for flowable resin composites. However, because these materials behave as non-Newtonian fluids, their flow properties vary widely under different shear conditions, and accurate interpretations of measurements remain beyond the expertise of most clinicians.

Flowable resin composites are formed by suspending solid ceramic particles in resin matrixes, resulting in viscoplastic fluids that can be characterized according to

yield stresses. Yield stresses of viscoplastic materials are defined as the required shear stress for initiation of flow, and also explain inhibition of flow under the relatively low stress induced by gravity. Thus, yield stress relates directly to fluidity, which is defined as flow by weight, and yield stress measurements using rheological methods have been used to evaluate the fluidity of suspensions of solid particles, such as ink, paint, cosmetic creams, food pastes, chocolates, and cement¹⁴⁻¹⁸.

The aim of this study was to develop an appropriate method for measuring yield stresses of flowable resin composites and to quantify fluidity and handling characteristics. The null hypothesis was that there is no significant difference in yield stress among flowable resin composites used in this study.

METHODS AND MATERIALS

Five commercial flowable resin composites were tested in this study: AliteFlo LV (AF: Bisco, Schaumburg, IL, USA), Flow-it ALC (FI: Jeneric/Pentron, Wallingford, CT, USA), Venus flow (VF: Heraeus-Kulzer, Wehrheim, Germany), Tetric N-flow (TF: Ivoclar-Vivadent, Schaan, Liechtenstein), and Revolution Formula2 (RV: Kerr, Orange, CA, USA) (Table 1).

Rheological measurements

Rheological measurements were performed using a viscometer (RE-215U, TOKI SANGYO, Tokyo, Japan) and a cone-and-plate module with a cone radius of 24 mm and a cone angle of $1^\circ 34'$. Diagram of the cone-and-plate rotational viscometer is shown in Fig. 1. The cone is driven by the motor at variable rotational speed and

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Table 1 Flowable resin composites and composition according to the manufacturer's information

Code	Brand name	Manufacture	Resin matrix	Filler content	
				Size (μm)	Load (wt.%)
AF	AliteFlo LV	Bisco, Schaumburg, IL, USA	Bis-GMA, TEGDMA	0.03–0.7	60
FI	Flow-it ALC	Jeneric/Pentron, Wallingford, CT, USA	Bis-GMA, TEGDMA, EBADMA	0.04–4	66
VF	Venus flow	Heraeus-Kulzer, Wehrheim, Germany	TEGDMA, EBADMA	0.005–5	62
TF	Tetric N-Flow	Ivoclar-Vivadent, Schaan, Liechtenstein	Bis-GMA, TEGDMA, UDMA	0.04–3	63.8
RV	Revolution formula2	Kerr, Orange, CA, USA	Bis-GMA, EBADMA	Ave. 0.6	60

Fig. 1 Diagram of the cone-and-plate rotational viscometer.

sample is sheared in the narrow gap between the cone and the plate. The resistance to the rotation of the cone, which is caused by presence of the sample, is measured by the torque measuring device. The shear stress can be calculated from this reading and the geometric constant of the cone. All measurements were performed at 25°C. Composites (1.1 mL) were extruded onto the plate as slowly as possible through a syringe with no needle. After residual stress was removed, composites were pre-sheared at a shear rate of 40 s⁻¹ for 3 s. This shear rate was determined by calculating the average shear rate of composites that were extruded through a syringe and needle with an internal radius of 0.4 mm at a volumetric flow rate of 3 mm³ s⁻¹. Accordingly, maximum wall shear rates of material flows through circular tubes can be calculated based on the internal radius of the tube and the volumetric flow rate using Eq. (1), which is derived from the standard Hagen-Poiseuille equation.

$$G_{\text{wall}} = 4Q/\pi R^3 \quad (1)$$

Here, G_{wall} is the maximum wall shear rate (s⁻¹), Q is the volumetric flow rate (mm³ s⁻¹), and R is the internal radius of the tube (mm).

Gregory¹⁹ showed that the average shear rate is two-thirds of the maximum wall shear rate using Eq. (2).

$$G_{\text{average}} = 8Q/3\pi R^3 \quad (2)$$

Here, G_{average} is the average shear rate (s⁻¹).

Pre-shearing times were determined by calculating residence times of composites in an 18-mm long needle during extrusion from a syringe. After pre-shearing, flow curves were obtained by measuring shear stress (Pa) at various low shear rates of 0.2–1.0 s⁻¹. To accommodate the time taken for the viscometer reach equilibrium, Shear rates were monitored until the observed values became stable, and the required time for measurements depended on both shear rates and flow properties of samples. All measurements were repeated three times for each material.

Determination of yield stress

Yield stress refers to the highest stress at which a material resists flow, that is, the stress at which the slightest increase in stress will initiate flow. Accordingly, in rheological analyses, yield stress can be defined as shear stress at a shear rate of zero. Experimental application of this definition gives accurate approximations of yield stress from plots of shear stress values over a range of shear rates followed by extrapolation of fitted mathematical models of flow curve data (Fig. 2). In this study, we employed the Casson model (Eq. (3)), which is a well-known rheological model that is suitable for viscoplastic fluids.

$$\sigma^{1/2} = \sigma_c^{1/2} + \eta_c^{1/2} \dot{\gamma}^{1/2} \quad (3)$$

Here, σ is shear stress (Pa), $\dot{\gamma}$ is the shear rate (s⁻¹), σ_c is the Casson yield stress (Pa), and η_c is Casson plastic viscosity (Pa·s).

A simple method for fitting data with the Casson

model involves plotting the square root of the shear stress *versus* that of the shear rate (Casson plot). The resulting linear plots facilitate extrapolation to the zero shear rate, and the yield stress is then determined as the square of the value at the intercept, which is obtained

Fig. 2 Schematic of the rheological method for determining yield stress.

Yield stress can be assessed by plotting shear stress values over a range of shear rates, followed by fitting of flow curve data to mathematical models and extrapolation to the stress axis.

by numerically extrapolating the Casson plot data to the stress axis. To assess how well the model fits the experimental data, the coefficient of determination (R^2) was calculated.

Determination of apparent viscosity

To compare the accuracy of yield stress and apparent viscosity measurements of fluidity, the apparent viscosity at the lowest shear rate (0.2 s^{-1}) was calculated from the rheological measurement according to Eq. (4).

$$\eta = \sigma / \dot{\gamma} \quad (4)$$

Here, η is apparent viscosity ($\text{Pa} \cdot \text{s}$), σ is the shear stress (Pa), and $\dot{\gamma}$ is the shear rate (s^{-1}).

Statistical analysis

Significant differences in yield stresses and apparent viscosity measurements were identified using Tukey multiple comparison tests. A p value less than 0.05 was regarded as indicating statistical significance.

RESULTS

All data from flow curves and Casson plots are shown in Figs. 3 and 4, respectively, and typical flow curves for

Fig. 3 Flow curves ($n=3$).

Fig. 4 Casson plots ($n=3$).

Fig. 5 Typical flow curves of shear stress *versus* shear rate (a) and typical Casson plots of the square root of shear stress *versus* the square root of the shear rate (b). Flow curves show that all samples have non-Newtonian shear-thinning behaviors. Casson plots were approximately linear for all samples.

shear stresses *versus* shear rates are shown in Fig. 5(a). In these analyses, all samples exhibited non-Newtonian shear-thinning behaviors. Moreover, Casson plots of the square root of the shear stress *versus* the square root of

the shear rate were approximately linear for all samples (Fig. 5(b)), and fitted well with the Casson model, as indicated by the R^2 values (Table 2). Obtained yield stresses and apparent viscosities are shown in Table 2.

Table 2 Yield stress, coefficients of determination (R^2) for the Casson model, and apparent viscosity of flowable resin composites

Code	Yield stress			Apparent viscosity at 0.2 s ⁻¹	
	Mean (Pa)	S.D. (Pa)	R^2	Mean (Pa·s)	S.D. (Pa·s)
AF	43.1 ^a	1.06	0.972–0.986	421.4 ^A	19.2
FI	33.3 ^b	2.55	0.975–0.992	436.3 ^A	9.6
VF	21.6 ^c	2.31	0.964–0.972	261.0 ^B	21.4
TF	14.9 ^d	1.19	0.989–0.993	289.3 ^B	7.3
RV	5.4 ^e	0.09	0.997–0.999	110.3 ^C	1.2

Different superscript letters for each column indicate a significant difference ($p < 0.05$)

Yield stresses ranged from 5.4 Pa for RV to 43.1 Pa for AF, and varied significantly between the five composites in the following order: AF>FI>VF>TF>RV. Meanwhile, apparent viscosity did not differ significantly between AF and FI, or between VF and TF, but varied from 110.0 Pa·s for RV to 436.3 Pa·s for FI in the following order: FI>AF>TF>VF>RV.

DISCUSSION

In this study, we assumed that yield stress measurements are applicable to flow properties of resin composites, and determined yield stresses by fitting the Casson fluid model to the flow curve data using a standard rheological apparatus comprising a simple cone-and-plate rotational viscometer. Although the flow property of conventional non-flowable resin composites would provide useful information for comparison, we evaluated only flowable resin composites because conventional composites had too high flow resistance to measure yield stress. The Casson model is based on a structural model of interactive behaviors of solid and liquid phases in two-phase suspensions. However, this model is only applicable when flow curve data fit well. In a preliminary study, the Herschel-Bulkley model, which is a well-known alternative to the Casson model, was used to calculate yield stresses from fitted data, but returned meaningless negative yield stress data and was deemed inappropriate for descriptions of flowable resin composites. However, the present R^2 values (Table 2) from the Casson model indicated sufficient accuracy of flow measurements of the present composites to be considered an appropriate basis for measurement.

During yield stress measurements of thixotropic materials such as resin composites, constant pre-treatments are essential. Moreover, a previous inter-laboratory study of yield stresses²⁰⁾ indicated that uniform sample preparation and conditioning procedures and well-controlled shear histories are critical for accurate and reproducible estimations. Accordingly, excess or deficient pre-treatments result in mismatches between measured values and the flow properties exhibited in actual clinical conditions.

Flowable resin composites are usually applied *via* extrusion from syringes with needle attachments, which compromise internal structure and change flow properties. Beun *et al.*²¹⁾ indicated the need for consideration of these effects and Lee *et al.*⁷⁾ controlled for the effects of shear history by measuring the slump of flowable resin composites after extrusion from a syringe using a custom-made loading device. Accordingly, in this study, sample pre-treatments were conducted carefully so that pre-shearing could be performed under conditions equivalent to the extrusion of flowable resin from a syringe. This approach may contribute to reproducibility and better agreement with actual clinical conditions.

Unlike previous rheological studies, in which the fluidity of flowable resin composites was evaluated according to viscosities under low shear conditions^{7,22)}, we evaluated fluidity using yield stress (defined as shear stress at a shear rate of zero) approximations from shear stresses at low shear rates of 0.2–1.0 s⁻¹. Because the shear rate of 0.2 s⁻¹ is close to the lower limits of common viscometers, flow curves of shear stress *versus* shear rate (Fig. 5(a)) showed no differences between shear stresses of AF and FI at the shear rate of 0.2 s⁻¹, suggesting no differences in apparent viscosities. Although these observations were confirmed in static analyses, the yield stress of AF was higher than that of FI and was similar for VF and TF. These results demonstrate that yield stress measurements can be used to detect differences in fluidity that cannot be shown using measurements of apparent viscosity at low shear rates. Hence, we conclude that yield stress measurements are more suitable than apparent viscosities for evaluating the fluidity of flowable resin composites. Furthermore, because the method can be performed using a simple viscometer and does not require the use of a costly rheometer, it is preferable as a standard method for evaluating the fluidity of flowable resin composites.

The yield stress of RV was much lower than that of the other four resin composites, indicating that RV has high fluidity and would have the most suitable handling properties for use as a restoration liner and as a pit and fissure sealant. However, although AF is categorized as a low-viscosity type by its manufacturer, it was

found to have the lowest fluidity among the materials tested and would therefore be useful for Class IV and V restorations.

Further studies are required to validate this method and determine reproducibility of yield stress measurements among different laboratories.

CONCLUSION

Given the comparative simplicity and precision of the proposed method for measuring yield stress, it should provide a useful indicator for selecting flowable resin composites with suitable handling properties for various clinical applications.

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