

Rheological characterization of dental resin composites – fundamental study and clinical applications

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*Even the mountains flowed
before the Lord.*

Judges 5:5, translated by M. Reiner
(Physics Today, January 1964, p. 62).

Aknowledgements

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Sébastien Beun, août 2009

Summary

While many publications concentrate on the characterization of the mechanical and physical properties of resin composites in order to guide practitioners in their material's choice according to particular clinical conditions there is only very scarce reference of studies on their rheological properties. The purpose of this work was to study the flow characteristics of resin composites before curing as an attempt to complete their physical and mechanical characterization.

A first part of this work presents a characterization study of composites focusing on the comparison of their mechanical properties and the characterization of their inorganic fraction. Such characterization, although giving much useful information for the prediction of composites performance, is insufficient to determine proper clinical indications to restorative materials.

The rheological study of resin composites first focuses on the viscoelastic properties of commercially available materials. It was shown that they exhibit complex rheological properties. They are non-Newtonian, viscoelastic materials. Their viscosity dramatically decreases as the frequency or rate of deformation increases, they show solid-like behavior at rest and their rheological properties are time-dependant in such a way that when they are submitted to flow, viscosity drastically decreases and takes many hours to return to its original value.

From there, an evaluation of the influence of each component, organic as well as inorganic, on the rheological properties of final materials was performed with the help of model experimental formulations. The complex flow properties that were demonstrated with commercial formulations were confirmed by the experimental ones. It was also shown that the inorganic particles, and in particular sub-micronic particles, are the determinants of the complex rheological behavior since they induce many types of interaction mechanisms with their surrounding environment that lead to time-dependant local rearrangements of the structure of materials.

Finally, a third part develops links from rheological properties to possible clinical implications. Different flowable resin composites and pit and fissure sealants were characterized mechanically and rheologically, and attempts of clinical indications based upon both their flow properties and their mechanical behavior were made. On the other hand, since rheology is time-dependent, mechanical properties were also investigated as a function of processing time. It was demonstrated that some materials present a progressive increase of

their dynamic elastic modulus as a function of time after deformation. This particular behavior is linked to the type of microfiller and nanofiller they contain but cannot be explained on the basis of their rheological properties alone.

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1. INTRODUCTION

1. Dentistry, Past and Present

Dental pathologies have remained quite similar throughout history of humanity. Decays, toothaches, abscesses and premature tooth loss were already documented in ancient chronicles. The time that dental art appeared is not known. However, there is wide proof of its existence among ancient civilizations. The first known dentist was an **Egyptian** named Hesi-Re (3000 B.C.) who was the chief dentist to the Pharaohs. Egyptians performed abscessed teeth drainages, teeth splinting and much more. **Hippocrates** (500 B.C.) accurately described the surgical steps of tooth extraction in one of his writings. **Etruscans** (400-100 B.C.) made the greatest contribution to mechanical dentistry. Numerous Etruscan bridges and crowns were found that are pretty much the same as those made up until 1870 when the dental engine was invented. The **Romans** borrowed their dentistry from the Etruscans and made some improvements.

After the fall of Rome and throughout the major part of the Middle Ages, magic and superstitious nostrums were the traditional cures up to **Albucasis**, a Spanish moor of Cordova (1013 A.D.). He described many instruments that were specifically designed for dental care. After him came the time of barber-surgeons who mainly performed extractions.

However, the first to mention the filling of teeth with a restorative material (gold foil) after excavating and shaping a tooth cavity is **Giovanni of Arco** (1484 A.D.), a professor of medicine and surgery at Bologna.

Then, many savants contributed to the knowledge of teeth and oral pathology. Leonardo da Vinci (15th-16th century), Vesalius (16th Century), Ambroise Paré (16th Century) are some of them.

The father of modern dentistry is **Pierre Fauchard** (18th Century) who wrote a complete work on dental art called "The Surgeon Dentist". He recognized the close relationship between oral and general health. He described the removal of all decays and suggested to fill cavities with lead.

But the first really effective conservative dental procedures appeared in the second half of the 19th century, thanks to the developments of anesthesia and dental engine. **G.V. Black** described scientific cavity preparation and extension for prevention in 1892. Three years later, in 1895, he developed the balanced **amalgam alloy** while Roentgen discovered the x-ray. For the first time, it was possible to restore cavities quickly and inexpensively in the general population. Although other restorative materials such as fold foil of gold inlays were

still in use, dental amalgam quickly gained interest and remained the predominant material to restore dental cavities throughout most of the 20th Century.

Even though amalgam is still developed and improved nowadays, many detractors would like to see it disappear from current practice. The reasons for that are numerous. Its silvery appearance is totally un-aesthetic and, although it is somewhat acceptable in posterior teeth, it is pretty awful when used on anterior restorations. But the major concern about amalgam is the presence of mercury. While it has been shown that mercury concentrations in urine and feces of people who have teeth restored with amalgam is higher than for amalgam free people, there is still no evidence that it can lead to adverse effects in the general population [1, 2]. But the controversy is regularly sustained by many individuals and groups who link a variety of illnesses to the presence of mercury from amalgam restorations, the media often giving credit to these allegations.

During the past century people progressively gave more importance to aesthetics and attempts were made to develop an alternative to amalgam. **Silicate materials** were introduced at the same period as amalgam but showed many drawbacks. Their lifespan was way shorter than for amalgam and they quickly discolored and dissolved in aqueous environment. Unfilled acrylic polymers were also used but unsuccessfully. In addition, both silicates and acrylic materials showed poor mechanical properties.

Then, mixtures of **epoxy resins** and aggregates of quartz or porcelain were introduced [3]. Results were encouraging but because of the slow curing of epoxy materials, they were only used as indirect restorative materials.

Around 1960, the first **resin composites** were commercialized after **R.L. Bowen** synthesized the Bis-phenol-A-Glycidyl dimethacrylate, commonly known as Bis-GMA [4, 5]. This monomer quickly became the ultimate reference and most of the resin composites that are commercially available nowadays still contain it as main monomer. The use of dimethacrylates resulted in a huge improvement of the clinical performances of aesthetics restorative materials because they allowed for better stability, higher mechanical properties, less dimensional variations and, last but not least, better aesthetics [6].

But if epoxy resins adhere spontaneously to most surfaces, dimethacrylate does not. As a consequence, at the same time as those materials appeared, **bonding techniques** were presented to achieve satisfactory retention of restorations. The first step of bonding development is without a doubt the alteration of the tooth surface by acid-etch, introduced by **M.G. Buonocore** in 1955 [7]. Then adhesives progressively appeared that improved the link between etch tooth surface and resin composite.

From the 60's to the present days, resin composites and adhesive dentistry in general have considerably evolved and have nowadays by far supplanted amalgam in our countries. Many researchers all around the world work each day at improving clinical performances of resin composites. A quick search performed on Pubmed, the search engine of the U.S. National Library of Medicine that gathers all available information on international scientific publications, with “dental resin composite” as keywords, gives out 580 international articles for the year 2008.

2. Resin composite

A composite, from the scientist's point of view, is a combination of at least two chemically different components, each of them keeping its own physical identity, with a distinct interface separating the materials [6]. The so-constituted composite shows properties that could not be observed from the components taken separately. This is called **synergy**.

2.1. Composition of a dental resin composite

From a general point of view, a dental resin composite is an assembly of an **organic resin matrix** where the polymerization process takes place and inorganic **filler particles** that are dispersed in the organic matrix and that give the final material its mechanical properties. In addition, a **coupling agent** allows for strong chemical interactions between the organic matrix and the inorganic filler particles.

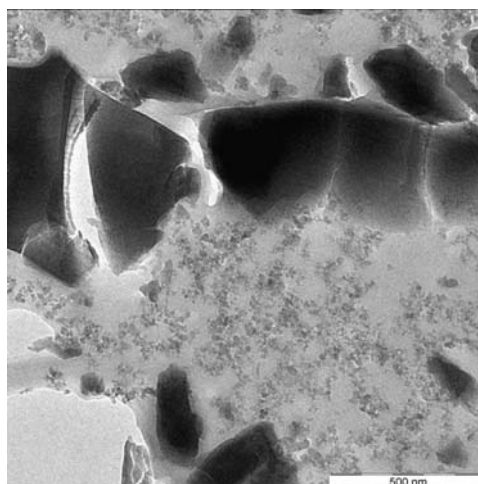


Figure 1-1: Transmission-Electron Microscopy (TEM) image of an experimental resin composite. Two types of inorganic filler particles (big and small) are dispersed in the organic matrix (in grey).

2.1.1. Organic matrix

The organic matrix is mainly made of **monomers** that are partially converted in polymers through the polymerization process. The molecules that are found in today's resin composites are usually based on methacrylate chemistry, whereas especially cross-linking dimethacrylates. The monomer that is the base of the development of resin composites is the 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane i.e. the **Bis-GMA**, formulated in 1956 by R.L. Bowen [4, 6]. It has been used extensively since, and is still the most utilized in current commercial formulations. The advantages of Bis-GMA are numerous. This difunctional molecule is superior to the more classical methyl methacrylate because of its large molecular size and strong structure, providing faster polymerization, lower volatility and lower polymerization shrinkage (6.1 % vol., about a third that of methyl methacrylate) [8, 9].

However, due to its high molecular weight (512g/mol), the viscosity of Bis-GMA is very high and lies between 500 – 800 Pa.s. at 23°C, which is too high for an efficient mixing with filler particles. Thus, the viscosity of Bis-GMA is lowered by admixture with dimethacrylate monomers of lower molecular weight in order to achieve a viscosity that allows for an optimal incorporation of filler particles. The molecule which is the most used for that purpose is triethyleneglycol dimethacrylate i.e. the **TEGDMA**. Indeed, with a molecular weight of 286 g/mol, TEGDMA has a viscosity of 0.1 Pa.s. at 23°C. In counter part of its lower viscosity, its lower molecular weight compared to that of Bis-GMA induces increased polymerization shrinkage (14.3 % vol.) [6, 9].

Other monomers are currently used, although not as often as those cited above. Urethane dimethacrylate (UDMA), ethyleneglycol dimethacrylate (EGDMA) or 2,2-bis[4-(2-methacryloyloxy-ethoxy)phenyl]propane i.e. Bis-EMA are some examples of monomers that are sometimes used in replacement of or in conjunction with Bis-GMA and/or TEGDMA.

The organic matrix also contains an **initiator-accelerator system** that allows hardening of the resin composites by polymerization of the monomers. Since nowadays composites are photopolymerized, they are nearly all using camphorquinone as photoinitiator. Accelerators that are the most often used are ethyl *p*-dimethylaminobenzoate (DMAB) or *N,N*-dimethylaminoethyl methacrylate (DMAEMA).

To achieve the longest possible storage and to prevent spontaneous polymerization, an **inhibitor** is used. Hydroquinone or butylated hydroxytoluene (BHT) are commonly used. In addition, stabilizers are used to ensure the stability of the polymerized material. Finally,

pigments are included to provide resin composites with shade that mimic the shades of natural teeth.

2.1.2. Inorganic filler particles

Different types and sizes of filler particles are used in the formulation of resin composites. Extensive scientific literature is available that shows the benefits of a maximum content of filler particles in resin composites [10, 11, 12, 13]. They provide clinically acceptable mechanical properties, they reduce polymerization shrinkage and wear and they have a lower thermal coefficient of expansion than that of dimethacrylate polymers. They also provide radiopacity which is of major interest in clinical practice and they participate to the aesthetic properties of the polymerized composite, influencing the translucency and fluorescence by the type and amount of filler used. Last but not least filler particles have a huge impact on the rheological properties of the final material [14, 15, 16].

Inorganic filler particles generally account for between 35 and 70 volume % or 55-85 weight % of the materials [12].

The filler particles are characterized by different compositions, different manufacturing techniques and different average sizes. The **macrofillers** have an average particle size between 0.2 and 5 μm . They are usually prepared by grinding big particles of radiopaque dental glass, quartz or ceramic. They are usually of irregular shape.

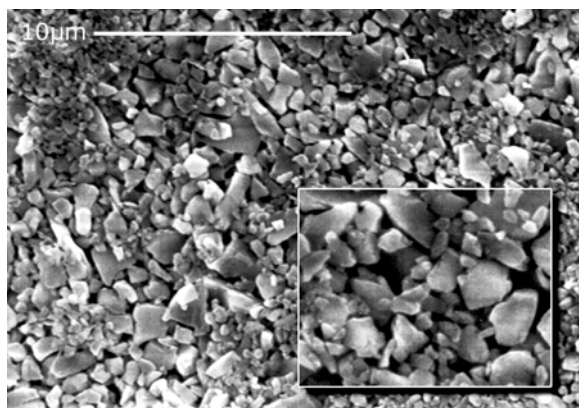


Figure 1-2: Macrofiller found in Grandio Flow (Voco, Cuxhaven, Germany) by Scanning-Electron Microscopy (SEM) after resin dissolution at 5000x magnification (10,000x in the insert).

The **microfillers** are particles with an average size of less than 0.1 μm . Fumed silica (i.e. pyrogenic silica) is very often used as microfiller in current formulations. Other microfillers are prepared via the sol-gel process [17]. They consist of primary particles of an average size of 5-100 nm. These particles were most often agglomerated but in new

formulation, isolated particles can be found too. In that particular case, they are qualified as **nanofillers**.

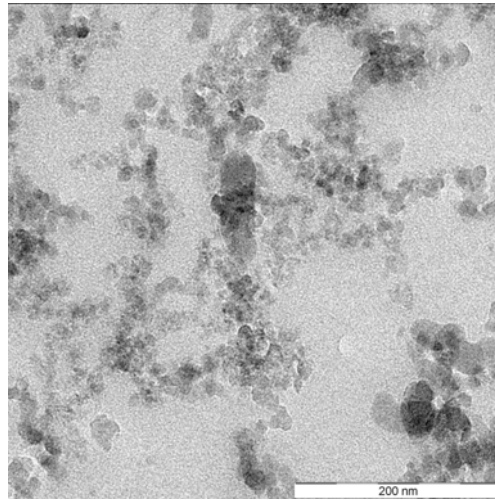


Figure 1-3: Agglomerates of fumed silica as observed by TEM. The average diameter of primary particles lies around 10 nm. The agglomerates can reach 50-150 nm in size.

In addition, **microfiller-based complexes** have been developed in order to achieve high filler loads. They are produced by polymerizing a resin matrix in which microfillers were incorporated and then milling it into particles of an average size of 10 to 100 μm . The inorganic part of a composite is usually made of about 70-80 % macrofiller and 20-30 % microfiller [9].

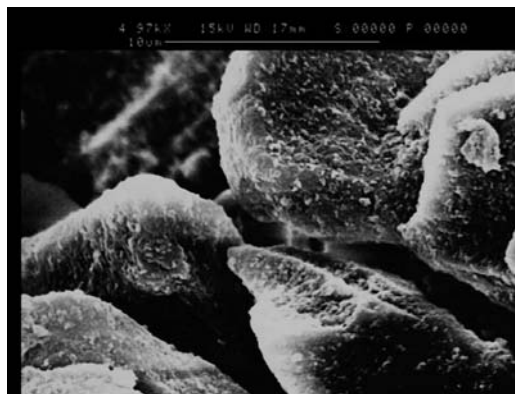


Figure 1-4: Microfiller-based complexes of the Durafill VS (Heraeus-Kulzer, Weillhrheim, Germany) observed by SEM at 5000x magnification.

It is to be noted that from a materials' scientist point of view, what dentists call macrofiller is in fact microfiller because its average diameter lies around 1 μm . Likewise, what dentists call microfiller is actually nanofiller because of their size that is smaller than 0.1

μm . Nevertheless, the dental classification of filler particles will be used throughout this work.

Moreover, an inorganic opacifier is generally added in order to provide composites opacity that is comparable to that of natural teeth. Most often, particles of titanium dioxide with an average size of $0.2\ \mu\text{m}$ are used.

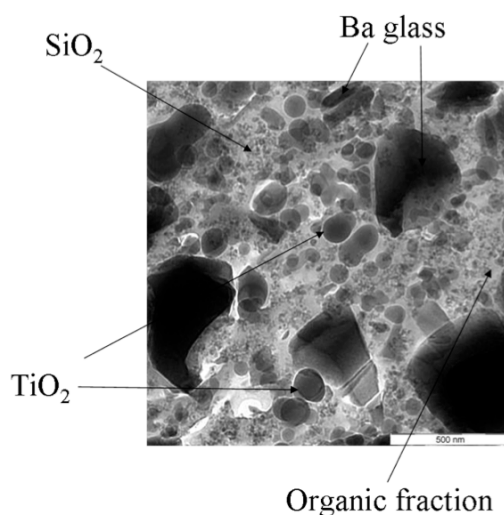


Figure 1-5: Grandio Flow (Voco, Cuxhaven, Germany) as observed by TEM. Ba glass is the macrofiller and silicon dioxide is the microfiller (aggregated) and the nanofiller (isolated). The opacifier (titanium dioxide) can also be observed.

2.1.3. Coupling agent

In order to obtain resin composites with good physical and mechanical properties, it is very important to link efficiently the polymer and the filler particles. But from a chemical point of view, the organic matrix and the inorganic filler particles are totally different. Indeed, the organic matrix is highly hydrophobic while the filler particles are highly hydrophilic. Coating the filler particles with a coupling agent is thus needed.

The molecules that are used are called alkoxysilanes or, shortly, **silanes**, which is a contraction of SILicon and methANE. Silanes contain two different functional groups. One is an alkoxy (Si-OR) that reacts with the Si-OH groups on the surface of the filler. The other, on the other side, is a Si-linked methacrylate group that is polymerized into the growing network of polymer during the photopolymerization. This allows for an effective chemical bonding of the filler particles to the organic matrix and thus, for a better cohesion of the polymerized materials resulting in better properties.

The two molecules that are the most often used are **MPMA** (γ -methacryloxypropyl-trimethoxy silane) and **APM** (γ -acryloxypropyl-trimethoxy silane).

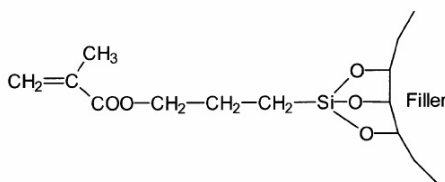


Figure 1-6: Representation of a silane bonded to the –OH groups on the surface of the filler. On the other side is the methacrylate group that reacts with the monomer.

In addition, non silanized microparticles are added that exhibit a very hydrophilic surface. In isolated form, they are highly unstable and they spontaneously link one to another via hydrogen bonds. This leads to the formation of irregular aggregates than can then form a particles' network throughout the entire composite [18]. That network drastically increases the viscosity of the resin composite and limits the maximum load of filler in the material [19]. Silanes are thus also needed in order to include as much filler as possible and to indirectly control the increase of viscosity induced by the particles themselves.

2.2. Classification of resin composites

Many properties of resin composites can be used as classification systems: clinical indications (anterior, posterior or universal), curing mode (self curing, light curing or dual curing) or viscosity (flowable, universal or packable). But the most popular classification system is based on the filler content of composites: macrofilled, microfilled and hybrids [20, 21].

2.2.1. Macrofilled composites

They were the first commercially available resin composites and appeared in the 60's. Nowadays they have almost disappeared because they present many drawbacks as compared to more recent formulations, the major one being very poor aesthetics. Indeed, their filler particles size ranges from 1 to 40 μm . This leads to a somewhat rough surface with low polishability.

2.2.2. Microfilled composites

Microfilled resin composites were introduced in the 70's in order to improve the aesthetic properties of dental restoratives. They contain silica (SiO_2) particles with an average diameter of 0.04 μm . But, since very small particles increase dramatically the viscosity of the material, only very small amounts of filler can be included. In order to increase the filler load

content of microfilled composites, prepolymerized particles are added. They are obtained by polymerizing aggregates of particles in a resin matrix and secondary grinding to diameters that range from 10 to 50 μm).

Because of the very small size of the filler, high polishability is obtained leading to very high aesthetics. But due to a limited inorganic filler load, the mechanical properties of microfilled resin composites are rather poor.

2.2.3. Hybrid composites

Hybrid resin composites appeared in the 80's. They represent the optimal compromise between durability and aesthetics. The majority of today's commercially available resin composites are hybrid composites. They contain a blend of different filler types and sizes, which allows for higher filler content and, as a consequence, higher mechanical properties.

Hybrid composites are subdivided in several groups: hybrids, microhybrids and nanohybrids. **Early hybrids** have almost disappeared. They contained fillers that had an average size of about 15 to 20 μm and very small amount of silica aggregates that had an average diameter from 0.01 to 0.05 μm . Throughout the years, grinding techniques have evolved and it is now possible to produce dental glass particles that sizes about 1 μm . Resin composites that contain such particles, coupled with silica aggregates are called **microhybrids**. The smaller particles as compared to early hybrids give the materials better aesthetic properties. In addition, it allows for a higher filler content, which improves the mechanical properties.

Recent improvements in filler technology, particularly the production of particles via the sol-gel process, allowed for the preparation of silica particles that are not aggregated anymore. Indeed, fumed silica aggregates very quickly during the preparation process due to high interactions via hydrogen bonds and coating with the coupling agent is performed subsequently. This leads to aggregates of silica particles that are layered with the silane. But in the sol-gel process, silica particles of diameters that range from 5 to 200 nm are coated in-situ, which drastically reduces interactions between particles and prevent aggregation [9, 17]. Resin composites that contain such particles, coupled with more traditional dental glass particles, are called **nanohybrids**. As a consequence, higher filler load is possible. This contributes to the reduction of polymerization shrinkage and, sometimes, improves mechanical properties. But the major advance with nanohybrid composites is the appearance of materials that combine good mechanical properties and excellent aesthetics. Indeed, the

size of nanoparticles is a fraction of the wavelength of visible light (0.4-0.8 μ m). As a consequence, they don't scatter that particular light, resulting in the human eye's inability to detect these particles [22]. This has tremendous implications for the optical performances of materials and surface polishability.

Up to a few years ago, most of commercially available resin composites were microhybrids. But today, more and more nanohybrids are commercialized that will supplant microhybrids in the near future.

2.2.4. Classification according to the viscosity

From a clinical point of view, resin composites should adhere to tooth tissues, should not adhere to instruments, should flow easily into big and small cavities but should not flow when no external force is applied i.e. they should not flow under their own weight in order to allow the practitioner to recreate the original anatomy of the restored tooth. This will be discussed thoroughly in the present work but it can already be stated that all these prerequisites are currently virtually impossible to obtain in one single composite. This is why manufacturers have developed materials with different viscosities so that dentists can choose composites that will suit a particular clinical condition the best.

Most of commercially available resin composites have a **universal viscosity** i.e. an all purpose viscosity. They are suitable for most clinical conditions, they are quite easy to insert in classical cavities and can be sculpted. However, for very small cavities as fissures, cracks or pit and fissure sealing, universal composites are not indicated because they are not able to flow correctly into cramped areas. **Flowable** resin composites were developed for such applications. Their lowered viscosity is obtained by modifications in the organic matrix by addition of a higher content of low viscosity monomers, and by slightly reducing the filler load. This results in higher flow capabilities but lower mechanical properties, higher polymerization shrinkage and higher stickiness, to tooth tissues but also to instruments.

As an attempt to reduce stickiness and to answer to many dentists that prefer the feeling of packing amalgam into cavities to that of modeling composites, **packable** resin composites were developed. They first appeared in 1997 and were produced with opposite modifications to those made to produce flowable composites. High viscosity monomers were privileged and the filler load was put to a maximum. Unfortunately, they are not truly packable as amalgam is and some of them showed catastrophic clinical performances [23].

It is to be noted that microhybrid, nanohybrid and microfilled composites can be either universal or flowable. Packable resin composites are almost exclusively microhybrids.



Figure 1-7: Resin composites are available with different viscosities: flowable (left), universal (center) and packable (right).

2.2.5. Classification according to clinical indications

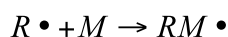
Requirements for restorative materials are not the same depending on the location of the tooth to be restored. Anterior teeth (incisors and canines) need materials that mimic the best natural tooth tissues so restorations cannot be seen but are not subject to very high mechanical loads. To the contrary, posterior teeth (premolars and molars) encounter very high mechanical loads but do not require very high aesthetics.

Universal resin composites are suitable for both anterior and posterior restorations. They combine good mechanical properties and satisfactory aesthetics. **Anterior** composites have very good aesthetic properties but, most of the time, slightly lower mechanical properties. They are usually available in many shades, combining both dentin shades and enamel shades so that the practitioner can control shade and translucency the best. On the other side, **posterior** composites are generally available in just one or two shade and have rather poor aesthetics but present higher mechanical properties.

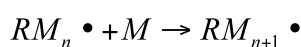
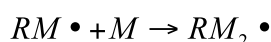
2.3. Photopolymerization

Most of today's resin composites are light-cured. Polymerization is then initiated by visible blue light. This is a free radical polymerization. The reaction takes place in three stages, called the **initiation**, **propagation** and **termination** stages [24].

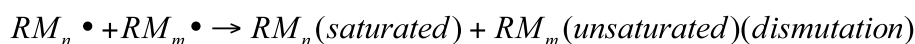
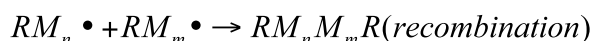
The reaction is initiated by a free radical ($R\bullet$) produced either with a peroxide-amine system or a diketone-amine system and exposure to visible blue light. This is very reactive and promptly reacts with nearby monomer (M) and initiates the polymerization process. The carbon-carbon double bond of the monomer splits and transforms the molecule to a carbon-carbon single bond and a free unpaired electron:



The initiation stage is followed by the rapid addition of other monomer molecules to the free radical that was transferred to the initial monomer. The free electron is shifted to the end of the growing chain:



This propagation reaction continues until the growing free radical is terminated. The termination stage may take place either by recombination, i.e. combination of two free radicals, or by dismutation, i.e. by transfer of a radical $H\bullet$ with production of unsaturated link on one of the two chains:



In addition, because light-curing takes place very quickly, many growing chains are trapped in the hardened materials without having terminated their reaction.

The free-radical polymerization of monomers with unsaturated double bonds does not result in all the double bonds reacting. The percentage of double bonds that effectively react and convert to single bonds is called the **degree of conversion**. Even in optimal laboratory conditions, the degree of conversion of composites that are cured with conventional light-curing units is rarely higher than 60 % [13].

Clinically, exposure times for polymerization vary depending on the type of light-curing unit and the type, depth and shade of the composite. Times may vary from 20 to 60 seconds for a 2 mm thick restoration. Microfilled composites require longer exposure than microhybrid composites because the microfillers scatter more light. Dark shades require more illumination than lighter shades or translucent shades. In order to achieve a clinically acceptable degree of conversion, successive layers of resin composites should not be thicker than 2 mm [13].

3. Evaluation and testing of resin composites

In order to be clinically efficient, resin composites must fulfill a series of properties that are directly linked to the particularities of the oral environment. To date, there is still no good understanding of the clinical factors and the magnitude of their effect in predicting long-term performance of resin composite restorations; the clinical challenges are strongly multifactorial and there are significant interactions among the factors [25]. There is a lack of hypothesis-driven *in vivo* studies to explore factors that may predict performance but there is a strong need to provide professionals valuable comparisons between materials in order to determine which of them would suit a particular situation the best. This is why *in vitro* studies make sense, even though there is a lack of studies that correlate laboratory tests with clinical performance. Indeed, *in vitro* studies allow researchers to understand and compare materials without the constraints of clinical trials. Laboratory tests are highly reproducible, fast and make comparisons between a wide variety of materials possible, which would be limited in clinical trials because of a lack of patients and teeth.

However, laboratory test results need to be compared to benchmarks that still need to be determined in *in vivo* studies. Indeed, clinical trials that flesh out the minimum or maximum test values that have a clinical significance still need to be carried out.

A non exhaustive list of clinical factors that may influence the performances of resin composites and their possible related laboratory tests is presented in Table 1-1.

Clinical factor	Materials tests
Marginal discoloration	Polymerization shrinkage, swelling, creep
Bulk discoloration	Color stability
Surface smoothness	Hardness, filler characteristics
Maintenance of anatomical contours	Wear, fatigue, solubility, fracture toughness
Placement and anatomical shaping	Viscoelasticity, surface energy, ambient light sensitivity
Curing time	Reaction kinetics, light transmission
Layer thickness for increments	Reaction kinetics, light transmission, depth of cure
Food and beverage contact	Solubility, color stability, wear
Temperature change	Color stability, thermal expansion
Bacterial contact and sec. caries	Solubility, bacterial growth promotion, antibact. prop.
Saliva contact	Water sorption, hydrolytic stability, enzyme degradation
Post-operative pain	Hydroscopic swelling, modulus
Allergy or toxicity	Biological activity
Appearance on radiographs	Radiopacity

Table 1-1: Clinical factors and possible relevant laboratory tests for evaluation of resin composites.

3.1. Mechanical properties

In the oral environment, resin composites are exposed to many mechanical challenges. These challenges can cause deformations. Thus, the mechanical properties of composites determine their ability to face these solicitations. They must be considered collectively because no single mechanical property can give a true measure of quality or performance. In addition, improving one property may compromise another.

3.1.1. Forces

A force is generated by one body that interacts with another. If the body remains at rest i.e. does not move or translate, the force causes the body to deform or change its shape.

A force is defined by three characteristics: **point of application**, **magnitude** and **direction**. The unit of force is the **Newton, N**.

In the oral environment, most of the forces that are encountered are **occlusal forces**. Occlusal forces between adult teeth are the greatest in the molar region, with forces on the first and second molars that range from 400 to 800 N. As a comparison, the average forces on the premolars, canines and incisors are about 300, 200 and 150 N, respectively [24].

3.1.2. Stress and strain

When a force is applied on a constrained body, a resistance is developed to this external force application. This resistance is a force that is opposite in direction and equal in intensity to the applied force. It is distributed over an area of the body and is thus often expressed as a force per unit area (stress = force/area) and is called **stress**, typically denoted as **S** or **σ**. The unit of stress is expressed as **Pascal, Pa** (1 Pa = 1 N/m²).

The stress varies proportionally with the force and inversely with the surface. The surface is thus an important consideration, especially in dental restorations where the surface on which force is applied is very small. As a numerical example, if a biting force of 400 N is applied on a small occlusal pit restoration of no more than 4 mm², the stress developed would be 100,000,000 Pa, or 100 MPa.

In general, individually applied forces may be axial (tensile or compressive), shearing, bending or torsional. All stresses, however, can be resolved into combinations of three types: tension, compression and shear (Figure 1-8).

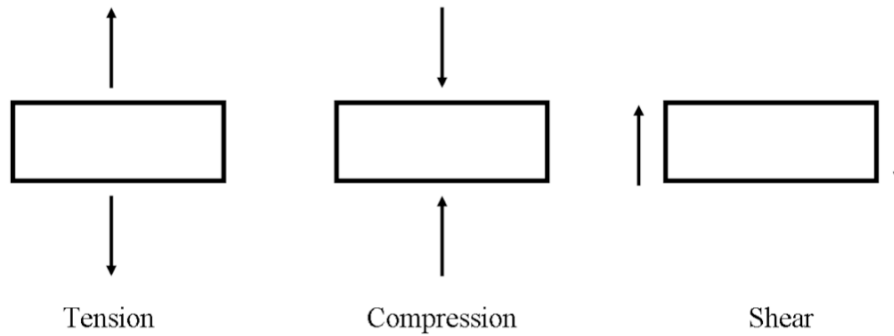


Figure 1-8: Types of stresses.

Tension occurs when a body is subjected to two sets of forces that are directed away from each other in the same straight line. It tends to pull an object apart. **Compression** results when the body encounters two sets of forces that are directed towards each other in the same straight line. **Shear** is the result of two sets of forces that are parallel from each other but in opposite directions and not in the same line.

Each type of stress is capable of producing a corresponding deformation. **Strain (ϵ)** is the change in length per original length:

$$Strain(\epsilon) = \frac{(L - L_0)}{L_0} = \frac{\Delta L}{L_0}$$

Strain is a unitless value. It is often reported as a percentage.

It is possible to plot on a graph the deformation that results of an applied force on a body to obtain a force-deformation curve. The problem is that, if the same force is applied on a second body made of the same material but with other dimensions, the resulting deformation characteristics change. However, if the force is normalized per surface unit and the deformation is normalized by the original dimensions of the object, the resultant is a **stress-strain curve** that is independent of the geometry of the body tested. This is therefore preferred to force-deformation curve, as it allows comparing materials themselves, and not bodies made of a specific material. A typical stress-strain curve provides a lot of information on the characterization of the mechanical properties of a material (Figure 1-9).

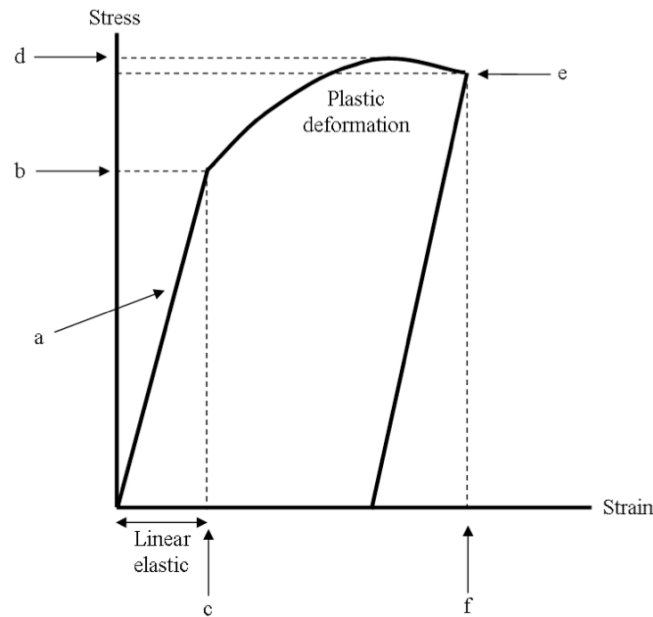


Figure 1-9: Typical stress-strain curve. The elastic modulus (slope of *a*), stress at elastic limit (*b*), strain at elastic limit (*c*), ultimate strength (*d*), fracture strength or stress (*e*) and strain at failure (*f*) can be observed.

ELASTIC MODULUS

The measure of elasticity of a material is described by the elastic modulus, also called Young's modulus when deformation is in extension or compression. It is denoted by the symbol **E**. It represents the **stiffness** of a material within the elastic range and is determined by calculating the ratio of stress to strain, which actually is the slope of the linear elastic portion of the stress-strain curve:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{\epsilon}$$

Because strain is unitless, the elastic modulus has the same unit as the stress, **Pascal (Pa)**.

ELASTIC LIMIT

The elastic limit is the maximum stress that a material can withstand without any permanent deformation. When the stress is removed, the body returns to its original dimensions. The strain that is associated with the elastic limit is called the **stress at elastic limit**. The region of the stress-strain curve that is before the elastic limit is called the elastic region. The region after the elastic limit is called the plastic region since the application of a stress greater than the elastic limit results in a permanent deformation of the body.

ULTIMATE STRENGTH

The ultimate strength is defined as the maximum stress that a material can withstand before failure.

FRACTURE STRENGTH

The fracture strength, or stress, is the stress at which a material breaks. It is to be noted that materials do not necessarily break at the point at which the maximum stress occurs. The **strain at failure** is the strain at which fracture occurs.

Other properties of materials are linked to stress-strain curves, while they are less often used to characterize resin composites. **Ductility** is the ability for a material to be drawn into wire when in tension. **Malleability** represents its ability to be hammered into thin sheets without fracturing. Finally, **toughness** is an indication of the amount of energy necessary to cause fracture of a material.

3.1.3. Other mechanical properties***FLEXURAL STRENGTH***

The flexural strength is obtained when a bar, simply supported, and not fixed, at each end is loaded with a load applied in the middle. Such test is called a **three-point bending test** and the maximum stress measured is the flexural strength.

FATIGUE STRENGTH

A body that has been subjected to a stress that is below the maximum elastic limit returns to its original state without any change in its internal structure or properties. However, when this stress is repeated a great number of times, the strength of the material may be dramatically reduced and, finally, cause failure. This repeated loading is defined as **fatigue**.

The fatigue strength is the stress at which a material will fail under repeated loading. It is thus dependant on the magnitude of the load and the number of load cycles. It is often represented as a stress (or strain)-number of loads curve.

DYNAMIC ELASTIC MODULUS

The dynamic elastic modulus (**E_D**) is defined as the ratio of stress to strain for small cyclical deformations at a given frequency and at a particular point on the stress-strain curve.

In general, elastic modulus that is calculated from a dynamic testing is higher than when calculated from a static testing.

HARDNESS

Hardness can be generally defined as the resistance to permanent surface indentation or penetration. It is then a measure of the resistance to plastic deformation and is measured as a force per unit area of indentation. In dentistry, it represents the ease of finishing of a restoration and its secondary resistance to in-service scratching. The most common methods of measuring hardness of restorative materials are the **Knoop** and **Vickers** hardness tests. They both depend on the penetration of some small symmetrically shaped indenter into the surface of the materials being tested. The tests differ in the indenter materials, geometry and load. A standardized load is applied to the indenter that penetrates the surface of the material. This results in a symmetrically shaped mark in the material that can be measured under a microscope and then related to tabulated hardness values. The dimension of the indentation varies inversely with the hardness of the material tested.

WEAR

Wear is a loss of material resulting from removal and relocation of materials through the contact of two or more materials. Wear is generally undesirable, but under controlled conditions, especially during finishing and polishing procedures for resin composite restorations, it is highly desired to some extent.

Wear in the oral environment is usually characterized by the loss of the original anatomy of the material. It can result from mechanical, physiological or pathological causes. Indeed, normal mastication can cause **attrition**, particularly in populations that eat unprocessed food. Put to a pathological extent, sliding of opposite teeth surfaces against each other is called **bruxism**. Also, tooth brushing with some “whitening” toothpastes can cause **abrasion** since these materials play their whitening effect by the highly aggressive filler particles they contain.

Wear can also result from attacks via chemically aggressive substances. Wear of teeth surfaces and restorations that result from pathological repeated vomiting (as anorexic patients do, for instance) is a typical example of **corrosive wear**.

Finally, **surface fatigue wear** is a consequence of surface or subsurface cracks in materials that are caused by stresses induced by asperities or free particles. Materials then break off under cyclic loading and sliding.

Multiple processes occur simultaneously in wear. As a consequence, its study and evaluation is not a simple task since it is very difficult to reproduce all the factors that contribute to it.

3.2. Physical properties

3.2.1. Optical properties

With the development of resin composites, the possibility for high aesthetics in restorative dentistry was born. To this end, resin composites with optical properties that mimic natural teeth very well are of high importance.

Many factors influence the way the human eye sees a particular object. The color and luminescence of everything is the result of either a reflexion of a transmission of the beam of white light, or just a portion of it. The way that white light is either reflected, scattered or transmitted through resin composites depends on many factors and, as an attempt to characterize the optical properties of composites, researchers analyze and try to compare their color, their translucency, their fluorescence and their metamerism properties to natural teeth.

The **color**, or hue, is the result of the combination of wavelengths of the visible light that are reflected, scattered or transmitted.

Translucency is the property of materials that allows the transmission of light but scatters it in such a way that object cannot be distinguished through it.

Fluorescence is the secondary emission of luminous energy of lower frequency by a material when a beam of light is shone on it. Sound human teeth emit fluorescent light when excited by ultraviolet radiation, the greatest intensity of the light emitted being in the blue region. The first commercially available resin composites were not fluorescent at all. Although restorations seemed undetectable for the human eye under normal light conditions, they appeared as big black spots under ultraviolet lights similar to those widely used in nightclubs. Today researchers attempt to match the fluorescence of resin composites to that of natural teeth.

Metamerism is the property by which two materials appear of identical color under a particular light source but of different color under another light source. Actually, metameric colors seem identical to the eye but are of different spectral energy distributions. As for the fluorescence, it explains why restorations can appear of high aesthetics under some light source and catastrophic under another.

3.2.2. Thermal properties

The oral environment is subjected to important and repeated temperature variations. From about 37°C at rest, teeth structures can be put in contact with materials that are either very cold (ice cream at around -5°C) or very hot (coffee or tea at around 50 to 55°C). A thorough knowledge of the thermal properties of dental materials is thus of primary importance in the success of restorations.

Thermal conductivity is defined as the quantity of heat passing through a body per unit area and per time unit. A large restoration close to the pulp may cause discomfort or even pain if the materials used has a high thermal conductivity. A good understanding of the conductivities of restorative materials is desirable to give the pulp the appropriate degree of thermal insulation, comparable with that of normal tooth. In addition to thermal conductivity, **specific heat** quantifies the energy that is needed to increase the temperature of a material by 1°C. The higher is the specific heat, the slower the temperature of the material increases. Strongly linked to those two properties is the **thermal diffusivity**, which is a measure of transient heat flow, i.e. it describes the rate at which a body with a non uniform temperature approaches equilibrium.

When a material is heated, it expands. Inversely, when it is cooled, it contracts. The change in length per unit length for a 1°C change in temperature is called the **linear coefficient of thermal expansion**. It differs from one material to another and may have considerable consequences in the success of dental restorations. Indeed, if the difference between the coefficients of thermal expansion of both tooth tissues and the restorative material is important, it may compromise the integrity of the margins of the restoration and/or induce cracks in both materials.

3.2.3. Viscoelasticity

As well as cured resin composites are solid, essentially elastic materials, uncured composites are viscoelastic i.e. they present both properties of liquid and solid materials. More extensive information on viscoelasticity is given in section 4. Rheology (page 24).

3.3. Chemical properties

Once they are placed in cavities, restorative materials still interact with a lot of chemically active liquids and solids. They may **tarnish** due to some surface reactions or **discolor** when in service because colored substances penetrate the material and/or continue chemical interactions. Resin composites may fail because of **water sorption**. Indeed, as water

penetrates the material, polymer chains may be forced apart, coupling agent may be destroyed and bonding to tooth tissues may be weakened, resulting in a rapid breakdown of the performances of the restoration. Another consequence of water sorption is that water acts as a solvent and thus increases the **release of different molecules** (i.e. leaching) into oral fluids.

But resin composites, as well as other restorative materials, are also chemically active during the storage period that precedes their clinical use, despite the fact that they contain stabilizers and polymerization inhibitors. This strongly influences their **shelf life**. Temperature, humidity, time of storage as well as the bulk of materials concerned and the type of container have a huge influence on the speed of deterioration of a material after it has been produced.

3.4. Biocompatibility

Any material that is placed in contact with the human body, directly or indirectly, must perform its desired function without eliciting any undesirable local or systemic effect to the body. This is called **biocompatibility**. In the specific case of resin composites, interactions between the material and its surrounding environment include hypersensitivity, cytotoxicity and allergy.

Resin composites are to be bonded to tooth tissues in order to exert their role properly. There is, unfortunately, evidence that bonding can be deficient to some extent. If a proper bond does not form, or if debonding occurs, saliva and everything it carries such as bacteria or food debris may penetrate the gap between the tooth and the restoration. Such **microleakage** is the major cause of postoperative sensitivity and, further, secondary decays.

Postoperative sensitivity and **hypersensitivity** result of an undesirable pulpal irritation. While postoperative sensitivity is mainly caused by operative procedures, hypersensitivity is more a consequence of the cytotoxic properties of the constituents of resin composites. Indeed, methacrylates, as well as many other molecules that are widely used in composites chemistry, have showed cytotoxicity *in vitro*. Moreover, after resin composites are cured, they still release various levels of components that have potential adverse effects on cells. Doses are very low however, and depend on many factors such as the quality of curing and the type of composite. Resin composites related cytotoxicity is moderate and significantly reduced within the 48 hours after curing and by the presence of a dentin barrier. Hence, light cured composites that are widely used nowadays are less cytotoxic than the older chemically cured ones.

In addition to cytotoxicity, constituents of resin composites are known to potentially cause **allergic reactions** by contact with skin or oral soft tissues.

From a clinical point of view, resin composites are extensively used for several decades and it is believed that they are safe when used properly. Cytotoxicity causes more the production of a reactional dentin barrier that provides additional protection to the pulp than a severe prejudice to pulpal cells; allergic reactions fortunately remain anecdotic. There is still no scientific documentation of adverse effects of resin composites to the human body today.

4. Rheology

Materials for which the effect of load application rate has no influence on the relationship between stress and strain are called **elastic**. Within their elastic limit, they recover their original state when an applied stress is removed. Cured resin composites are essentially elastic. But before they are polymerized, they need to be modeled in order to give them adequate adaptation to tooth tissues and satisfactory anatomy. This is only possible because the application of a stress leads to a permanent deformation. Materials in this state are **fluids** instead of solids. The science that studies the flow behavior of materials is called **rheology**.

4.1. Viscosity

The flow characteristics of liquids differ from one material to another because they offer various resistances to a same stress. The resistance of a fluid to flow is defined as the **viscosity**.

Consider two parallel plates separated from each other. The space between the plates is filled with the liquid to be analyzed:

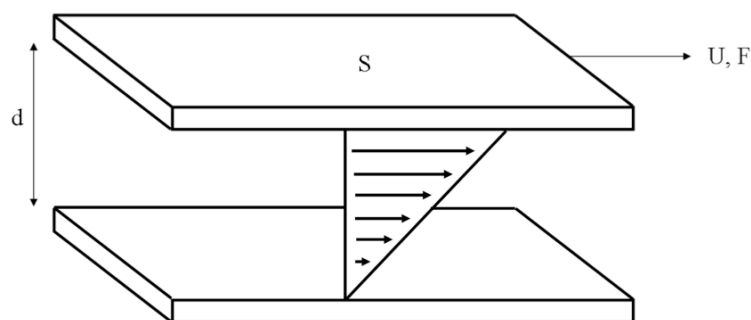


Figure 1-10: Laminar shear of fluid between two plates. The friction between the fluid and the moving plates causes the fluid to shear.

The shear stress τ that is necessary to generate the movement is expressed as follows:

$$\tau = \frac{F}{S}$$

where F is the force that is applied and S the surface of the plates. The resulting shear rate is determined by:

$$\dot{\gamma} = \frac{U}{d}$$

where U is the relative speed and d the distance between the plates. The link between the shear stress and the shear rate is expressed following the Newton's law:

$$\tau = \eta \cdot \dot{\gamma} \quad \text{or} \quad \eta = \frac{\tau}{\dot{\gamma}}$$

where η is the viscosity of the material tested. The unit of viscosity is **Pascal.second**, Pa.s, but data are still often reported in poise, p, or centipoise, cp (1 Pa.s = 10 p = 1000 cp). For illustration purpose, Table 1-2 gives the approximate viscosity of some familiar materials at room temperature:

Material	Viscosity (Pa.s)
Glass	10^{40}
Molten glass (500°C)	10^{12}
Asphalt	10^8
Molten polymers	10^3
Honey	10^1
Glycerin	10^0
Olive oil	10^{-1}
Water	10^{-3}
Air	10^{-5}

Table 1-2: Approximate viscosity of some familiar materials at room temperature.

4.2. Newtonian and non Newtonian behavior

4.2.1. Newtonian fluids

Newton's law describes the flow of an ideal liquid. Such liquid is named a Newtonian fluid and its behavior presents the following characteristics [26]:

- the sole stress generated by shear is the shear stress,
- the shear **viscosity remains the same whatever the shear rate**,
- the **viscosity remains the same whatever the shear time** and the stress in the fluid disappears as soon as shear is stopped,

- viscosities measured using different deformation systems are proportional one to another, proportionality depending on the geometry of the flow.

The flow curve of a Newtonian fluid, i.e. the shear stress-shear rate curve, is a straight line. The slope of this line is the viscosity of the fluid, which remains constant whatever the shear rate. This is shown in Figure 1-11.

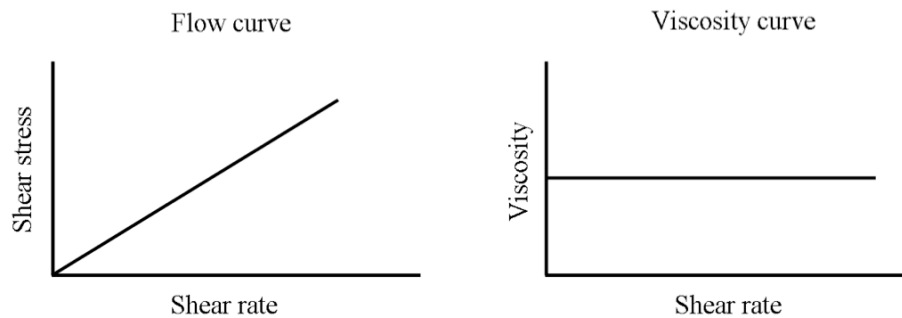


Figure 1-11: Flow curve and viscosity curve of a Newtonian fluid.

4.2.2. Non Newtonian fluids

A fluid that shows any deviation from that particular behavior is qualified as a non Newtonian fluid. There are three main deviation types from Newton's law: shear-thinning fluids, shear-thickening fluids and viscoplastic fluids [27].

SHEAR-THINNING FLUIDS

Fluids that give a viscosity that decreases with increasing shear rate are called shear-thinning. Such fluids usually show a constant viscosity at very low shear rates and very high shear rates. These regions are called Newtonian plateaus. Shear-thinning fluids are numerous: molten plastic, yoghurt or blood are some examples.

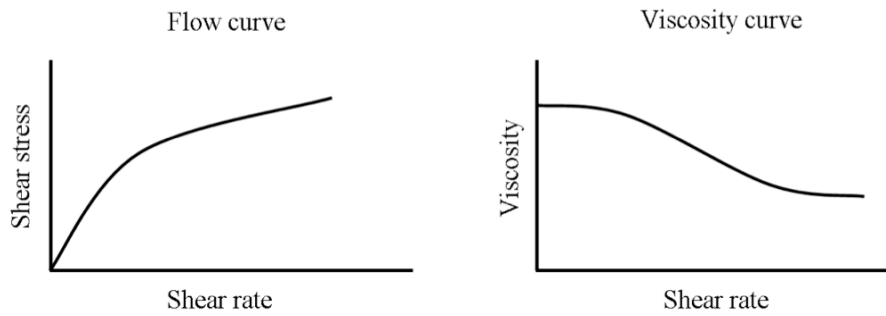


Figure 1-12: Flow curve and viscosity curve of a shear-thinning fluid. Two Newtonian plateaus can be observed on the viscosity curve, indicating regions of constant viscosity.

SHEAR-THICKENING FLUIDS

Shear-thickening fluids are fluids that show a viscosity that increases with an increased shear rate. They are by far less common than shear-thinning fluids. Some concentrated suspensions such as starch suspensions may sometimes show shear-thickening effect.

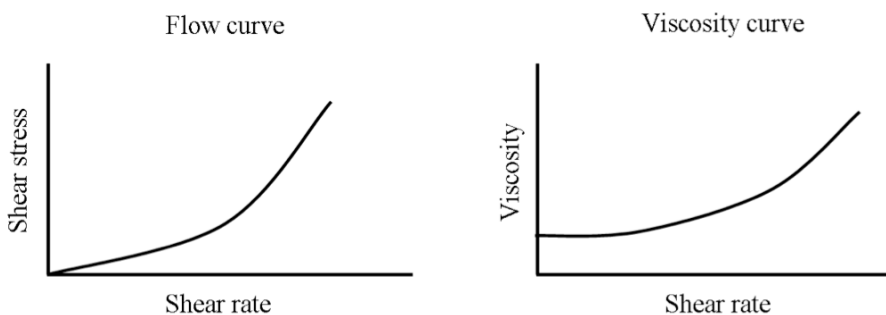


Figure 1-13: Flow curve and viscosity curve of a shear-thickening fluid.

VISCOPLASTIC FLUIDS

Viscoplastic fluids, also called Bingham plastics, are materials that show little or no deformation up to a certain level of stress. Above this **yield stress**, they flow readily. Once they flow, they can show either Newtonian or shear-thinning characteristics. House paints, mayonnaise and ketchup are good examples of viscoplastic materials.

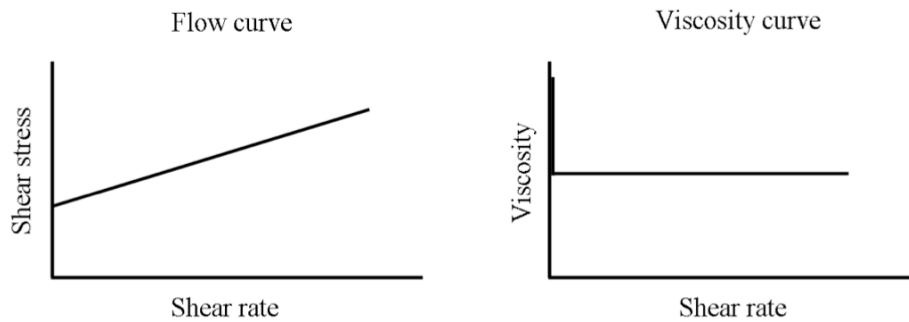


Figure 1-14: Flow curve and viscosity curve of a viscoplastic fluid with Newtonian characteristics once flow occurs.

4.3. Viscoelasticity

Some materials present a behavior which is **in between elastic solid and viscous fluid**. Such materials, when an applied load is suddenly removed, recover part of the deformation instantly, more with time but some permanent deformation remains. This time dependent response is called viscoelasticity [27]. A common way to measure this phenomenon is by **stress relaxation**. Indeed, when a viscoelastic fluid is subject to a step increase in strain, the stress relaxes in an exponential manner. If a purely viscous liquid is subjected to the same strain, the stress relaxes immediately to zero as the strain becomes constant. An elastic solid shows no relaxation at all. This is shown in Figure 1-15.

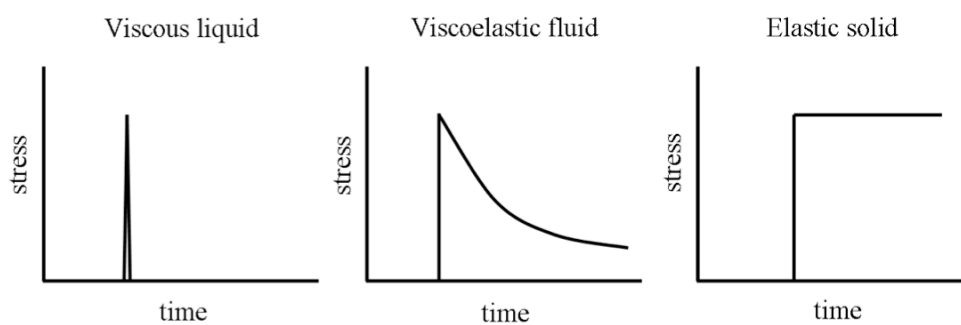


Figure 1-15: Stress response versus time of a purely viscous liquid, a viscoelastic fluid and an elastic solid to a step input in strain.

The relaxation time of a viscoelastic fluid may be modeled by the **Maxwell element**: a spring combined with a dashpot. Depending on the speed of application of the stress or strain, the response of the material will depend more on the response of the spring (if the stress is applied quickly) or the response of the dashpot (if the stress is applied slowly). For

very complex viscoelastic materials, rheological behavior can be explained by the generalized Maxwell model, which is a parallel combination of simple Maxwell elements.

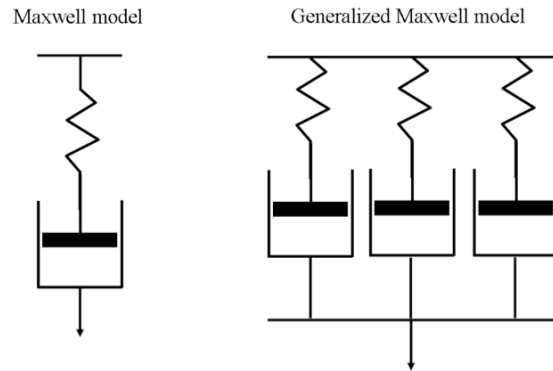


Figure 1-16: Simple Maxwell element represented by a spring and a dashpot (left). Generalized Maxwell model represented by a parallel combination of simple Maxwell elements (right).

The spring of the Maxwell model represents the elastic (solid) part of the material while the dashpot represents its viscous (liquid) part. Every Maxwell element has a characteristic relaxation time, which represents the time required for the stress in a stress relaxation experiment to decay to e^{-1} (0.368) of its initial value. Materials that have low relaxation times flow easily and as such show relatively rapid stress decay. On the other hand, materials with long relaxation times can sustain relatively higher stress values. Thus, whether a viscoelastic material behaves as an elastic solid or a viscous liquid depends on the material response time and its relations to the time scale of the experiment or observation. What really matters is the ratio between a material's characteristic relaxation time to the characteristic flow time. This is what rheologists call the **Deborah number**¹, De :

$$De = \frac{\lambda}{t}$$

where λ is the characteristic relaxation time of the material and t the characteristic flow time. If De is very high, the material behaves purely elastic. If De is very low, it behaves purely viscous. In between, the material behaves viscoelastic.

Depending on the deformation level and rate, the response of a viscoelastic material is drastically different. If the strain is very low or applied very slowly, the material will show a **linear viscoelastic response**, i.e. the viscosity will remain independent of the shear rate. To

¹ The origin of the Deborah number is indicated in the frontispiece to this manuscript, which was taken from the song of Deborah after her victory over the Philistines.

the contrary, if the strain is high or applied quickly, the material will show a **nonlinear viscoelastic response**, i.e. the viscosity will be a function of the shear rate and strain. This is illustrated in Figure 1-17.

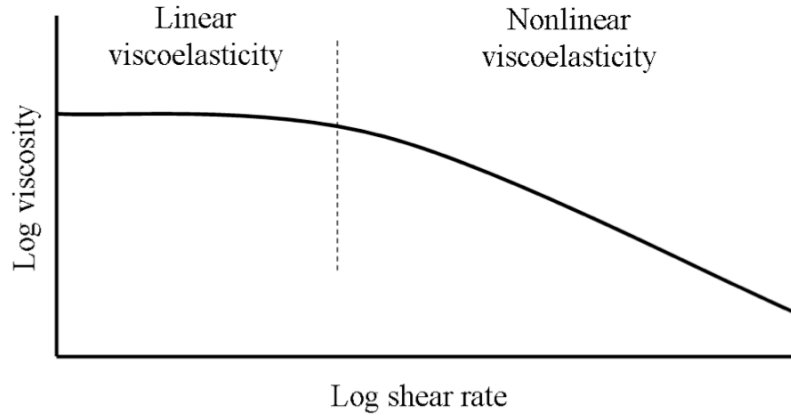


Figure 1-17: Linear and nonlinear viscoelasticity.

4.4. Thixotropy

Some non Newtonian shear-thinning fluids show a time-dependent change in viscosity. The longer the fluid undergoes a shear stress, the lower its viscosity. This phenomenon is called **thixotropy**. A thixotropic fluid shows a decrease in viscosity over time at a constant shear rate while a simple shear-thinning fluid displays a decrease in viscosity with increasing shear rate.

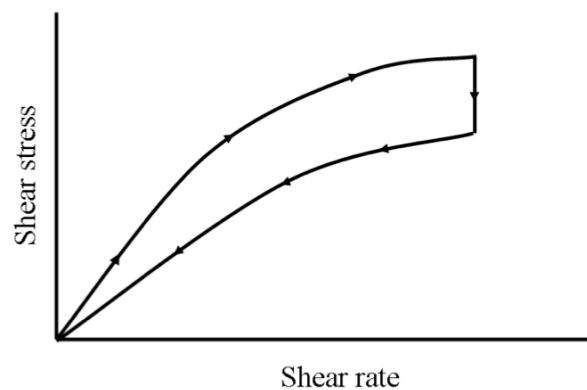


Figure 1-18: Flow curve of a thixotropic fluid. A decrease in viscosity at a constant shear rate is observed.

Thixotropy is a characteristic that is often shown by suspensions, i.e. liquids in which particles of various natures are dispersed (solid particles, tiny liquid droplets etc.). The rheological properties of suspension are a consequence of their internal structure in a three dimensional network and their heterogeneity at a microscopic scale [27, 28, 29, 30]. There are many factors within the microstructure of products, which determine the rheological properties, such as colloidal interactions between dispersed components, the junctions between structural elements, the properties of the structural elements, the interfacial behavior between phases and the structure of individual component phases. In addition, rheological properties are affected by the size of particles aggregates, they morphology and orientation.

Yoghurt is a basic example of a thixotropic material. When stirred, its viscosity usually decreases and, when put at rest for a few hours, grows up to its original value. Some clays and muds may show thixotropy too. In the industry, many kinds of inks exhibit thixotropic qualities.

Some fluids are anti-thixotropic: a constant shear stress for a time causes an increase in viscosity. This phenomenon is called **rheopexy**. Rheoplectic fluids are not common at all. Some lubricants may show rheoplectic properties.

4.5. Measuring the rheological properties of materials

Rheometers are instruments that study the particular flow properties of fluids. Many of them were developed with different characteristics in order to allow scientists to study a wide variety of materials with drastically different viscosities and rheological behavior. Capillary, concentric cylinder (called “Couette”), cone and plate, plate and plate as well as uniaxial extension are the most common measurement geometries used. Moreover, fluids may be analyzed in a steady or in a **dynamic** manner.

This section gives the basic concepts of dynamic deformations and a short introduction on dynamic oscillatory rheometers that were used in this study to characterize resin composites.

4.5.1. Dynamic system

In dynamic mode, the strain γ applied to the sample varies sinusoidally. Within a few cycles of start-up, the stress τ will also oscillate sinusoidally at the same frequency but shifted with a phase angle δ with respect to the strain wave. This is illustrated in Figure 1-19 and may be expressed mathematically as follows [27]:

$$\gamma = \gamma_0 \sin \omega t$$

$$\tau = \tau_0 \sin(\omega t + \delta)$$

where ω is the angular frequency and δ is a phase shift.

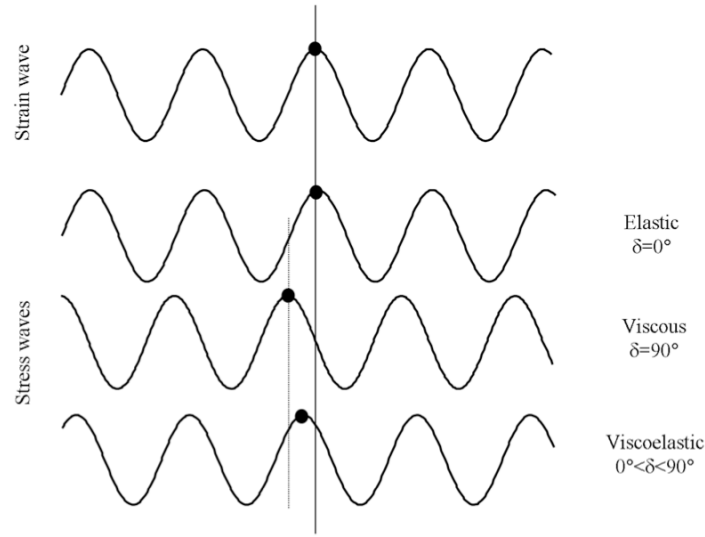


Figure 1-19: Sinusoidally oscillating shear strain produces a sinusoidally oscillating shear stress. The phase shift between strain and stress depends on whether the material is purely elastic, purely viscous or viscoelastic.

Such data are analyzed by decomposing the stress wave into two waves of same frequency, one in phase with the strain wave ($\sin \omega t$) and one 90° out of phase ($\cos \omega t$):

$$\tau = \tau' + \tau'' = \tau'_0 \sin \omega t + \tau''_0 \cos \omega t$$

It can be shown that:

$$\tan \delta = \frac{\tau''_0}{\tau'_0}$$

Such decomposition of the stresses suggests two **dynamic moduli**, G' and G'' (following Hooke's law):

$$G' = \frac{\tau'_0}{\gamma_0} \quad \text{and} \quad G'' = \frac{\tau''_0}{\gamma_0}$$

Where G' is the in-phase or elastic modulus and G'' is the 90° out of phase or loss modulus. We can also write:

$$\tan \delta = \frac{G''}{G'}$$

It is useful to represent the dynamic modulus in complex number notation.

G^* may be defined as:

$$G^* = G' + iG''$$

Where G^* is a complex number with G' as its real and G'' as its imaginary parts.

Hence:

$$\tau_0 = |G^*| \gamma_0 \quad \text{and} \quad \tau = G' \gamma_0 \sin \omega t + G'' \gamma_0 \cos \omega t$$

There is in fact nothing really imaginary about G'' . It is actually a measure of the energy that is dissipated per cycle of deformation per unit volume. This is why it is called the **loss modulus**. To the contrary, G' is a measure of the energy that is accumulated in the materials per cycle of deformation per unit volume. This is why it is called the **storage modulus**. G' and G'' are then respectively a measure of the elastic response and a measure of the viscous response of a material.

Another way to view the same experiments is in terms of a sinusoidal strain rate instead of sinusoidal strain. Then a **dynamic viscosity** material function is defined from the same type of development. A **complex viscosity** η^* is defined with a real part (viscous) η' and an imaginary part (elastic) η'' :

$$\eta' = \frac{\tau_0''}{\dot{\gamma}_0} = \frac{G''}{\omega} \quad \text{and} \quad \eta'' = \frac{\tau_0'}{\dot{\gamma}_0} = \frac{G'}{\omega}$$

The complex viscosity is:

$$\eta^* = (\eta' - i\eta'') = \frac{G^*}{i\omega}$$

Thus, dynamic shear measurements may either be expressed in moduli or viscosities. The two representations are completely equivalent. From a practical point of view, data that are most often reported are the complex viscosity, giving frequency dependent information on the resistance to flow, as well as the two moduli and $\tan \delta$ that provide useful information on the elastic or viscous characteristics at a given frequency.

4.5.2. Cone and plate and parallel plates rheometers

Dynamic oscillatory rheometers are devices that measure the dynamic rheological properties of materials, using various geometries, usually cone and plate or parallel plates. They may work either in strain controlled or stress controlled modes. Strain controlled rheometers induce a given strain in the samples and record the stress response and other stress-related parameters while stress controlled ones induce a given stress and record the resulting strain.

The **cone and plate** geometry is the easiest to describe. The sample is placed between a plate and a cone of a low angle which tip virtually touches the plate at the centre.

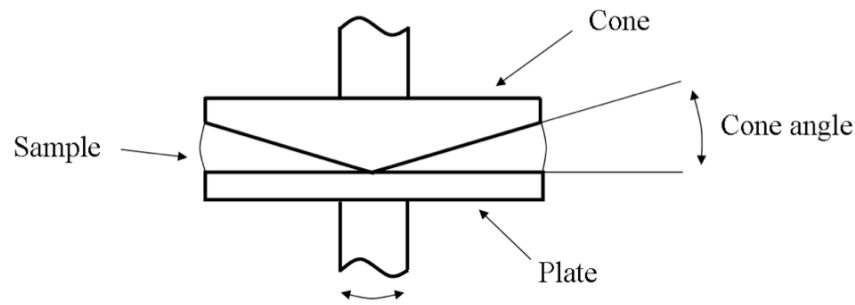


Figure 1-20: Cone and plate geometry for dynamic oscillatory rheometers.

The lower plate is coupled with a motor that makes the plate oscillate while the upper cone is coupled with a transducer that records the torque necessary to prevent the upper shaft from rotating. A mathematical processor calculates the dynamic moduli and viscosity parameters. The advantage of the cone and plate geometry is that because the cone ensures a progressive thickness of the fluid as a function of distance from the rotation axis, the shear rate is constant throughout the sample, which simplifies the mathematical analysis. But its drawback is that for filled materials, filler particles that are near the centre of the geometry may interfere with the movements of the plate by touching both the cone and the plate and act as a wedge. When such phenomenon is observed, or for very high viscosity materials, a parallel plates geometry must be preferred.

The **parallel plates** geometry works on the same principles as for the cone and plate geometry, except that the mathematical analysis is a bit more complex because the shear rate inside the material is not constant. The shear rate is maximal at the edges and close to zero near the centre.

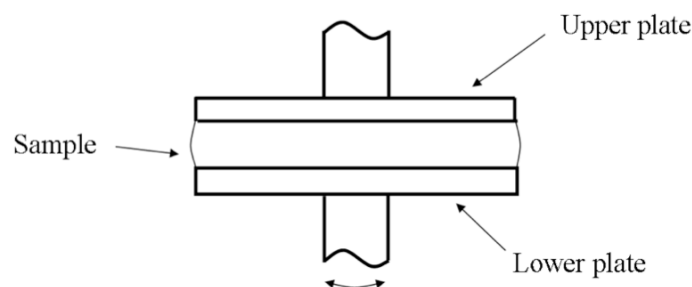


Figure 1-21: Parallel plates geometry for dynamic oscillatory rheometers.

4.6. Rheology for dental resin composites: state of the art

From the physicist's point of view, resin composites are highly filled suspensions of inorganic particles in an organic matrix, which provides these materials viscoelasticity, i.e. they have both liquid-like and solid-like behavior. Such suspensions also usually exhibit complex rheological properties such as shear-thinning (i.e. the viscosity decreases as the shear rate increases), thixotropy (i.e. the viscosity depends on the time) or yield stress (i.e. the materials does not flow if the applied stress is insufficient) [31, 32]. These properties can be very useful for the practitioner if they are correctly "tuned" but, so far, they are not or only poorly controlled.

Throughout the years, only few researchers have studied the viscoelastic properties of resin composites. In 1983, Ferracane et al. [33] used a rotational cone and plate viscometer to determine the viscosity changes of chemically cured composites during curing and, as a consequence, their working time. In 1993, Papadogiannis et al. [34] measured the temperature dependence of the viscoelastic properties of chemical and light cured composites after polymerization. The same year, Rubbi et al. [35] measured the viscosity changes of light cured composites with a home made oscillatory viscometer in order to determine their curing time. In 1996, Opdam et al. [36] compared the consistency of several resin composites by a press method. They found huge differences in the apparent consistency of composites from different manufacturers. They also found that the consistency of a composite was thinner when taken through a syringe tip than when taken directly from the syringe. In 1998, Taylor et al. [37] measured the viscosity of unfilled mixtures of Bis-GMA and TEGDMA with a rotational viscometer and determined their maximum filler load with a division-recombination test derived from the Eames setting time test for dental amalgam [38]. In 2003, Feilzer et al. [39,40] determined that the polymerization rate of Bis-GMA/TEGDMA composites is indicative of the viscoelastic behavior during curing: the higher the reactivity, the higher the stiffness and viscosity development.

But the most complete rheological characterization of resin composites before curing available at the time this work was started, in 2004, was made by Lee et al. in 2003 [41]. They characterized viscoelastic properties using a dynamic oscillatory rheometer and found that the viscoelasticity of composites in the same class is significantly different between brands and that the rheological properties may influence their handling characteristics. In 2006, Mesquita et al. [42] analyzed the viscoelastic properties of composites after polymerization by dynamic mechanical analysis (DMA). The same year, Lee et al. [43] studied the rheological properties of composites with variations in monomer and filler

composition using a dynamic oscillatory rheometer and found that the rheological properties of composites are greatly influenced by the formulation of the monomer and filler. Finally, in 2007, Lee et al. [44] used a vertical oscillation rheometer to investigate the viscoelastic properties of commercially available resin composites but that technique did not provide much more information on the rheological properties of composites than the previously used dynamic oscillatory rheometer.

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2. OBJECTIVES AND STRATEGY

1. Overview of the problem

In today's restorative dentistry, resin composites are by far more popular than silver amalgams. Indeed, many efforts at improving their physical, mechanical and aesthetic properties have been undertaken since the very first dental resin composites were developed and recently commercialized resin composites show clinical performances that are totally acceptable [1, 2] while offering high aesthetic possibilities that silver amalgam does not. In terms of longevity, studies that were conducted 10 to 15 years ago showed longevity of amalgam restorations (that are the ultimate reference in longevity of dental restorations) that were more than twice the longevity of composite restorations [3, 4, 5]. More recent studies tend to show that the longevity of composite restorations is improving, although there are wide variations in the results [2].

A lot of studies are conducted on the development of new monomers [1, 6, 7], new filler particles and surface treatments [1, 8, 9], new photoinitiation systems [10] and many other fundamental topics. Recent research on composites have allowed to reduce polymerization shrinkage, improve hardness, elastic modulus and fracture toughness while improving aesthetics by offering practitioners a wide variety of shades and opacities.

However, although properties of dental resin composites after they have been cured have considerably improved, only very few research concentrate on their properties before curing. Indeed, placing composites in dental cavities still presents many drawbacks. They are sticky and often tend to adhere more to instruments than to tooth tissues, compromising the quality of the margins of restorations [11]. Equally, in order to minimize the polymerization shrinkage as well as to improve the mechanical properties, the filler load is maximized. As a consequence, the viscosity of the resulting materials is very high, which makes the placement and modeling often a complicated task. Moreover, recent filler particles that are used in the so-called anterior composites are smaller than in the past in order to improve their optical properties and, as the specific surface of such particles is huge, their addition in composites dramatically increases the viscosity.

As an attempt to minimize these drawbacks, manufacturers have developed resin composites with different viscosities (see page 12). Although it allows a better management of most of the clinical situations, it does not solve the problem. Unfortunately, the alteration of composites' formulations in order to minimize a disadvantage often has the consequence of emphasizing another. For example, flowable resin composites are commercialized to face situations where the use of a universal composite is not possible, for placement in very small

cavities or cracks and fissures. But, because of a lower filler load and, very often, modifications in the composition of the organic matrix, flowable composites are more sticky and difficult or impossible to model properly. In addition, their mechanical properties are lower than those of universal composites and their polymerization shrinkage is slightly higher [12]. Likewise, packable composites present many drawbacks in terms of handling and mechanical properties as compared to universal composites [13].

Another attempt to minimize the clinical drawbacks of resin composites while continuing to improve their clinical performances in terms of mechanical properties as well as aesthetics is the incorporation of nanofillers in their inorganic fraction. Indeed, it is hardly conceivable for a composite to meet both the functional needs of a posterior Class I or II restoration and the superior aesthetics required for anterior restorations. Old microfillers, that were used in order to improve aesthetics, could be added to composites in only very small amounts because of the huge increase of viscosity they induced. Nanofillers, that manufacturers claim to have only limited impact on the viscosity of composites, can be added in higher amounts than for microfillers, resulting in anterior or flowable composites with increased filler content and, as a consequence, better performances [14].

2. Objectives and strategy

In this context, a thorough comprehension of the viscoelastic properties of resin composites is of utmost importance. The rheological properties of uncured materials govern the way they flow and thus the way the practitioner handles them. This is directly related to the ability of the resin composite to be correctly placed and shaped in cavities without formation of gaps between the material and the cavity margins or between successive layers of the restoration. Moreover, it conditions the possibility for the dentist to recreate the original anatomy, and as a consequence the function, of the restored teeth. All these factors play a huge role in the final success of a resin composite restoration. Unfortunately, the viscoelastic properties of today's commercially available composites are essentially an unintended consequence of their formulations. Indeed, manufacturers develop materials with the aim of producing composites with high mechanical properties and high aesthetics and the rheological properties are not controlled much. Their flow characteristics are obtained by trial and error rather than by a good comprehension and control of the influence of each component.

While many publications concentrate on the characterization of the mechanical and physical properties of resin composites in order to guide practitioners in their material's choice according to particular clinical conditions [12, 13, 15, 16], there is only very scarce

reference of studies on their rheological properties. The purpose of this work is to study the flow characteristics of resin composites before curing as an attempt to complete their physical and mechanical characterization.

A **first part** of this work presents a characterization of commercial composites in line with state of the art literature. Such characterization, although providing useful insight for predicting the performance of resin composites, appears insufficient in order to determine proper clinical indications to restorative materials. Therefore, a **second part** thoroughly characterizes the rheological properties of commercially available materials in order to understand what really happens when composites are submitted to flow when placed in cavities. From there, an evaluation of the influence of each component, organic as well as inorganic, on the rheological properties of final materials, is performed with the help of model experimental formulations. Finally, a **third part** develops links between rheological properties and possible clinical implications by correlating rheological and physical properties of commercially available composites.

This work is an attempt to bring a thorough scientific knowledge of the mechanisms that rule the particular flow properties of resin composites. It should help the development of future formulations with rheological properties that no longer are the result of trial and error but the consequence of a controlled influence and interaction of their components. This would thus allow formulating composites that are easier to place and model properly while retaining adequate mechanical performance.

In addition, if novel filler particles that have only a limited influence on the viscosity are developed, both universal and flowable materials with even higher filler load would be produced with the consequence of exhibiting improved mechanical properties and reduced polymerization shrinkage.

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3. OVERVIEW

1. Traditional characterization of dental resin composites (Chap. 4)

In vitro characterization of resin composites is a very common process in dentistry [1, 2, 3, 4]. Indeed, although laboratory tests only provide partial information on the behavior of materials, their advantages are numerous as compared to *in vivo* studies. Due to the huge amount of commercially available materials and their relatively low lifetime on the market, clinical studies with sufficient benefit of hindsight are difficult to manage and, once they are published, a significant portion of the materials tested are already replaced by new formulations by the manufacturers. In addition, the clinical success of restorations is multifactorial and, as it is linked with material-related properties, it is also linked with dentist-related and patient-related properties which are not or only poorly controlled in clinical trials [5]. *In vitro* studies provide partial solutions to these drawbacks. Laboratory tests are realized much faster than clinical experiments and allow researchers to deliberately choose the parameters on which comparisons are made, all the other parameters remaining unchanged. Thus, although *in vitro* studies do not give information on dentist- and patient-related factors that influence the success of dental restorations, they provide strong, reliable information on the properties of one material as compared to another.

The real challenge of *in vitro* experimentation on dental restorative materials lies in determining the clinically relevant laboratory tests and as there is still today no good understanding of the clinical factors and the magnitude of their effect in predicting long-term performance, it is not a simple task. However, tests results can be used to screen new materials against benchmarks to be determined in clinical trials in order to determine the minimum or maximum test values that have clinical significance. And, if today these benchmarks are still unclear, laboratory tests are of high interest and their clinical relevance is obvious.

As dental restorations are submitted to high mechanical constraints, **mechanical tests** are widely used to screen new materials. Wear, fatigue tests as well as polymerization shrinkage measurements are typical too since they are logically linked to resin composites' restorations failure. And, as these previous characteristics are known to be influenced by the filler particles, the **inorganic fraction** of composites is often characterized in terms of filler load and morphology.

In Chap. 4, nine commercially available resin composites were characterized on the basis of their mechanical properties (dynamic and static moduli of elasticity, flexural strength and Vickers microhardness), the morphology of the filler particles and their filler weight

content and finally their photopolymerization sensitivity as a function of the depth of cure. Among the materials tested were one nanofilled, two nanohybrid, four microhybrid and two microfilled composites.

Results for the static moduli of elasticity of the materials tested are presented in Figure 3-1. An optimal tooth restoration should mimic structural, mechanical and physical characteristics of dentin and enamel [4]. Xu et al., while measuring the elastic modulus of human enamel and dentin, obtained mean values of 19 GPa and 94 GPa respectively [6]. Since values calculated are lower than that of dentin and by far lower than that of enamel, it can reasonably be assumed that materials that present the highest modulus of elasticity will behave the best in clinical conditions. It is to be noted that difference between materials are huge and that different types of composites (nanohybrid, microhybrid and microfilled) present different value ranges.

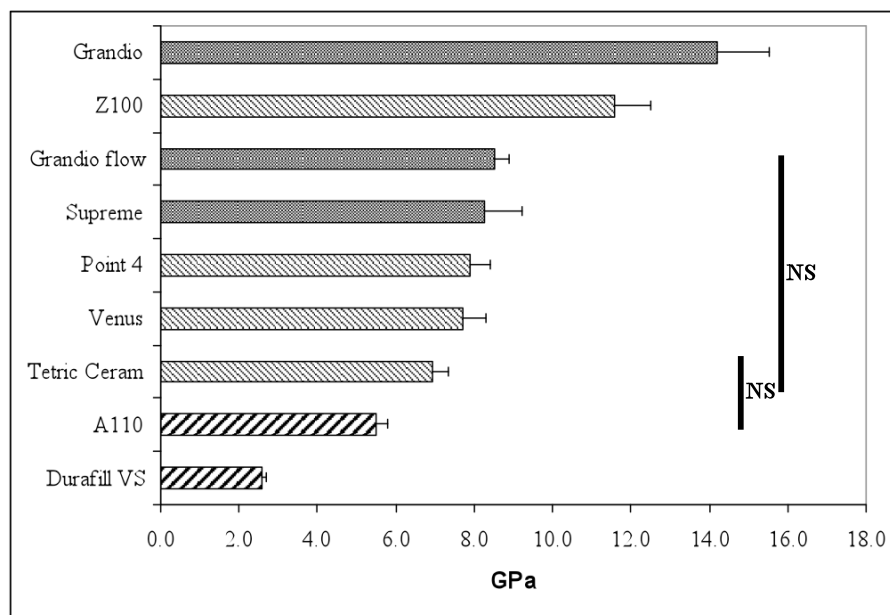


Figure 3-1: Static moduli of elasticity of the materials tested. Vertical bars connect materials that are not statistically significant ($p < 0.05$).

As for the moduli of elasticity, the filler load of resin composites may noticeably vary from one to another and different types of composites exhibit different ranges of filler loads, which may have dramatic influence on the final physical and mechanical properties of the materials. Results are presented in Figure 3-2.

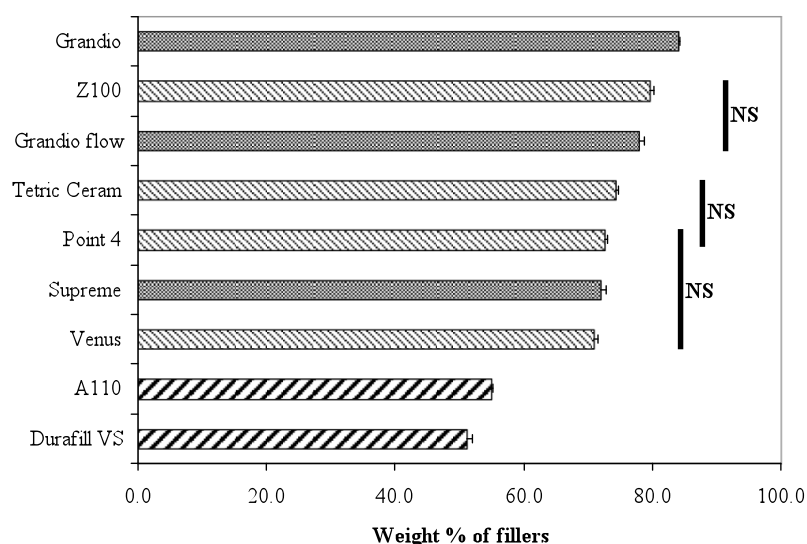


Figure 3-2: Mean values and standard deviations of the weight percentage of filler of the composites determined by thermogravimetric analysis. Vertical bars connect values that are not statistically significant ($p < 0.05$).

In addition to mechanical properties and filler weight content, the morphology of the particles and the polymerization sensitivity as a function of the depth of cure widely differ from one material to another. As stated previously, these differences implies that materials will have drastically different behavior when used in clinical conditions and, indirectly, that some composites are more suited for one type of clinical situation and others to other types of clinical situation. For example, microfilled composites are traditionally used for class V restorations where aesthetic properties are appreciated while the mechanical solicitations are put to a minimum. Microhybrid composites are much more used for posterior restorations where mechanical constraints are much higher. However, with the development of nanofillers, it now becomes possible to reconcile excellent aesthetics with high mechanical properties, and thus to use materials with broadened clinical indications.

2. Rheological study of resin composites (Chap. 5 & 6)

As mentioned in Chap. 1, resin composites are highly filled suspensions of inorganic particles in an organic matrix. Such materials usually exhibit complex rheological properties and a viscoelastic response to deformation. The rheological behavior governs the way resin composites flow and thus the way the practitioner handles them. Indeed, consistency and flow characteristics are directly related to the ability of the material to be correctly placed and shaped in the cavity without the appearance of gaps between the restorative material and the cavity margins or bubbles between successive layers of the restoration. Rheology also dictates

the ability of the material to be shaped in order to recreate the original anatomy, and thus the function, of the restored teeth.

Unfortunately, although many other physical and mechanical properties of resin composites are commonly studied in *in vitro* studies, rheological characterizations are exceptional and often limited to basic consistency measurements [7]. However, the interest of a thorough study of the way resin composites flow and, secondly, of the factors that dictate their rheological properties seems quite evident from a practical point of view.

2.1. Rheological properties of flowable resin composites and pit and fissure sealants (Chap. 5)

Among all the resin-based dental materials that are commercially available, those for which the interest of studying the flow characteristics is the most obvious are indisputably flowable resin composites. Indeed, their clinical handling is mainly based on the controlled flow of the material in tooth cavities of tiny dimensions, or even small fissures and cracks. In this context, pit and fissure sealants may be associated to flowable composites as “particularly flowable” resin composites and, again, their clinical performance highly depends on their ability to flow correctly inside pits and fissures of occlusal surfaces to form, once they are cured, an effective hermetic seal of these very high caries-susceptible areas.

It is widely known that there are very wide differences in the consistency of flowable resin composites from one manufacturer to another [8]. There is therefore a need for a classification of these materials based upon their real flow characteristics in order to determine in which clinical situation a material is best suited; a very low viscosity material must be chosen when one wants to seal pits and fissures but one may prefer to use resin composites with higher consistency in order to achieve a correct filling of small class V cavities.

In order to understand the flow behavior of these materials, rheological measurements were performed using a dynamic oscillatory rheometer. A parallel plates geometry was used for the flowable composites while a cone and plate geometry was used for the pit and fissure sealants due to their extremely low viscosity. Since all the rheological measurements were performed in the linear range of deformation of the materials, it was not a problem to switch geometries because in this particular situation results remain independent of the geometry used [9, 10]. In addition to rheological measurements, the inorganic fraction was characterized by thermogravimetric analysis (TGA) and by scanning-electron microscopy (SEM) to determine the weight percentage and morphology of fillers for each material tested.

All the materials tested show a complex rheological behavior. Their complex viscosity decreases dramatically as the frequency increases, indicating a strong non Newtonian, **shear-thinning** behavior. There is no hint of a Newtonian plateau even at the lowest frequencies. For flowable resin composites, the difference in the complex viscosities between low and high frequencies lies globally around two to three decades, which is a huge difference. For pit and fissure sealants, this difference is lower, around one decade. Complex viscosities versus frequency for the flowable composites are presented in Figure 3-3.

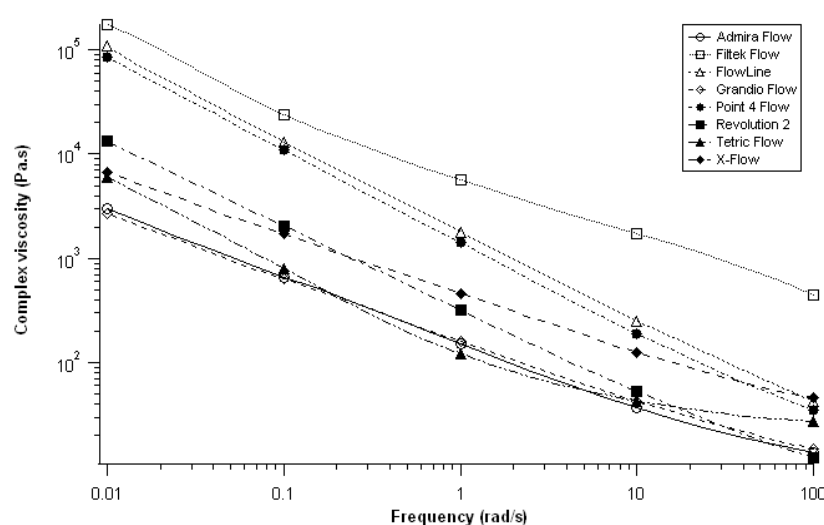


Figure 3-3: Complex viscosity (η^*) vs. frequency for the flowable resin composites tested.

In addition to complex viscosities results, storage moduli reveal a very strong elasticity of the materials tested, as evidenced by their very low slopes at low frequencies (except for Admira Flow, Grandio Flow and X-Flow). Storage moduli versus frequency are shown in Figure 3-4. These observations, in combination with the results of complex viscosities measurements, indicate that there is no transition to “Newtonian liquid flow” (called “terminal behavior” in technical terms) even at the lowest frequencies.

The rheological properties of pit and fissure sealants are pretty much the same as those of flowable resin composite except that values are lower. They are clearly shear-thinning materials and do not show any sign of terminal behavior.

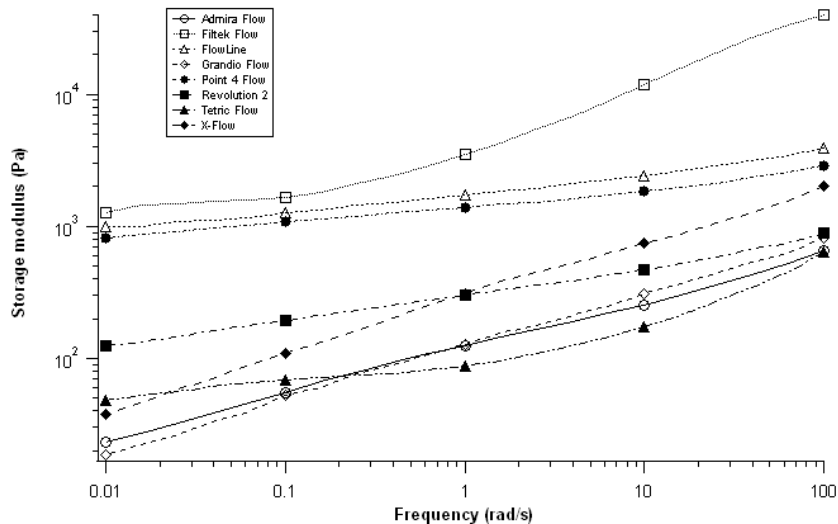


Figure 3-4: Storage modulus (G') versus frequency of the flowable resin composites tested.

From the results of the complex viscosity and the storage modulus versus frequency, three types of rheological behavior may nevertheless be distinguished. The first category, including Filtek Flow, FlowLine and Point-4 Flowable, groups materials that exhibit higher viscosities and storage moduli than the others. In addition, the slope of their storage moduli at low frequencies is close to the horizontal, indicating a very strong elasticity and thus strong solid-like behavior. The second category, including Revolution Formula 2 and Tetric Flow, shows materials that present lower viscosities than the first one, but whose storage moduli indicate the same elasticity and solid-like behavior than for the first category. Finally, the third category (Admira Flow, Grandio Flow and X-Flow) exhibit properties that are similar to materials included in the second category except that the slope of their storage moduli at low frequencies is higher, indicating less solid-like behavior than for the other materials tested. As a consequence, they are more likely to flow under their own weight than the composites included in the two first categories, which are less subject to creep flow. Regarding these results, the concept of flowable resin composite becomes relative.

No correlation could be made between the weight percentage of filler particles and the complex viscosity of the materials tested. No correlation could be made between the morphology of the filler particles and the complex viscosity of the materials either, which is in accordance with the results obtained by Lee et al. [11].

The evolution of materials viscosity as a function of time was also investigated. The principle is that resin composites were submitted to high shear flow (which is clinically the case when materials are placed using syringe's application tips) and then their viscosity was

monitored at very low frequency and very low strain over time. Results are presented in Figure 3-5.

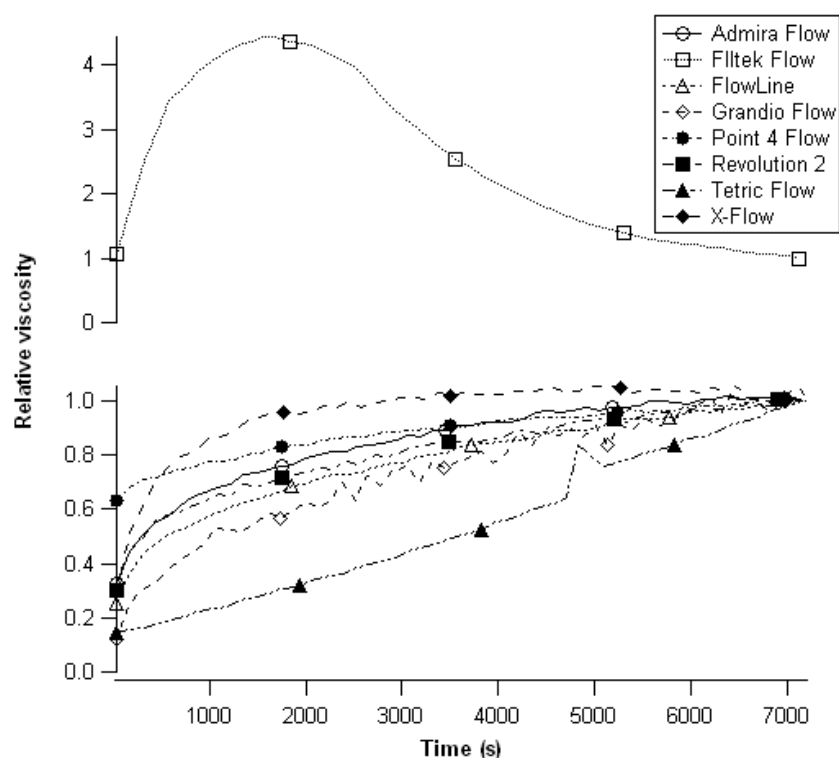


Figure 3-5: Relative viscosity of the flowable resin composites as a function of the time after deformation (the 1 value is the viscosity of the sample without any prior deformation).

Results show that the flowable resin composites tested clearly exhibit **thixotropy**. When destructured, their viscosity may drop down to less than the half of its nominal value and takes up to two hours to return to equilibrium. The overshoot observed for Filtek Flow is not clearly explained but suggests a jamming phenomenon indicating that its inorganic fraction must be very close to the maximum packing limit.

It is possible to characterize mathematically the return to equilibrium of resin composites as a function of time by a quite simple transformation in order to isolate a time constant τ . Results of the transformation and time constant of the materials tested are shown in Figure 3-6 and Table 3-1, respectively.

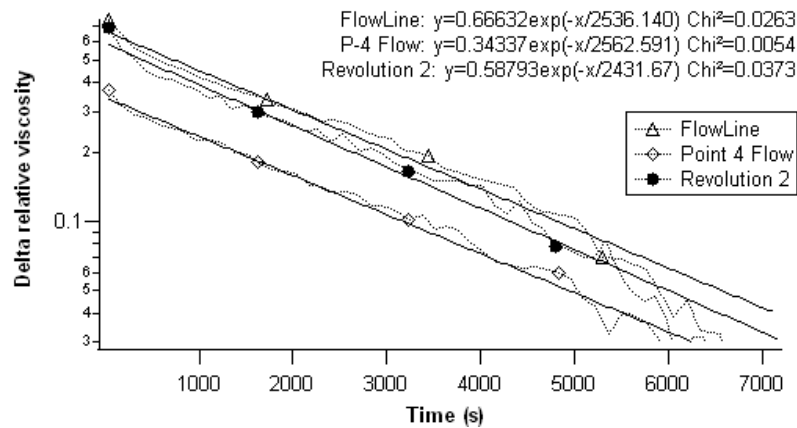


Figure 3-6: Modeling of the return to equilibrium of the flowable resin composites as a function of the time after deformation.

Material	Complex viscosity (Pa.s) at 0.1 rad/s		Time constant
	t = 0 s	t = 7,200 s	τ
Admira Flow	304.73	939.18	1822.16
Filtek Flow	30286	28344	N/A
FlowLine	3692.43	14718.4	2536.14
Grandio Flow	86.977	740.16	2492.21
Point-4 Fl.	6817.75	10792	2562.59
Revolution F.2	832.75	2757	2431.67
Tetric Flow	141.53	968.06	4098.86
X-Flow	706.79	2420.4	583.77

Table 3-1: Complex viscosity (η^*) as a function of the time after destruction of the flowable resin composites tested. Right column shows the calculated time constant of each material.

As no correlation could be made between fillers and complex viscosities, no correlation could be made between fillers morphology or load in weight and thixotropy. Indeed, four of the eight resin composites tested show similar time constants although the characteristics of their inorganic fractions are very different.

For the pit and fissure sealants tested, no thixotropy could be observed because due to their lower viscosities as compared to those of flowable resin composites, values recorded during the thixotropy tests were below the measurement threshold of the rheometer. Anyway, there is no reason to think that pit and fissure sealants do not show thixotropy as their composition is similar to that of flowable resin composites and their dynamic rheological properties are somewhat similar, too.

The viscosity of a resin composite is influenced by both the organic and the inorganic fraction. The type and ratio of each monomer used are directly responsible for the basic viscosity of the organic matrix. This one is then strongly influenced by the amount, shape, size and surface treatment of the filler particles that are added to the material [10]. The final material thus presents the complex flow properties that are presented above. However, there is no indication so far of the influence of each component on its final rheological behavior, which understanding is of utmost importance if one wants to control and modify the flow properties of a composite in order to better suit a particular clinical situation.

2.2. Rheological properties of experimental Bis-GMA/TEGDMA flowable resin composites with various macrofiller/microfiller ratio (Chap. 6)

As complex rheological properties were demonstrated for commercially available materials, this part of the work concentrated on the study of experimental formulations in order to evaluate the influence of each component, organic as well as inorganic, on the rheological behavior of resin composites. Unfilled mixtures as well as filled experimental composites were used. Rheological measurements were performed using dynamical rotational and oscillatory rheometers. Transmission electron microscopy (TEM) was also performed to characterize the morphology and spatial organization of the filler particles.

Unfilled formulations were classical mixtures of Bis-GMA and TEGDMA. The results showed that Bis-GMA, TEGDMA and all the mixtures of both components behave in a Newtonian way, which is in accordance with the results previously found by Lee et al. [12]. Viscosity decreases dramatically as the Bis-GMA/TEGDMA ratio decreases, which is what was expected since the role of TEGDMA in resin composites formulations is precisely to lower the viscosity of the organic matrix to a level that allows incorporation of a satisfactory amount of filler particles [13, 14].

Experimental resin composites were formulated in order to mimic the range of viscosities that are encountered for flowable materials. To this end, Bis-GMA/TEGDMA 50/50 mixtures (w/w) were prepared. They were filled at 60 wt% with two types of filler particles: silanized dental glass as macrofiller (with an average particle diameter of 1 μm) and partially hydrophobic fumed silica as microfiller (with an average aggregates length of 0.1 μm). Ratio between the two types of particles were respectively 60/0, 57/3, 55/5, 52/8 and 50/10 of the total weight of the samples.

The addition of inorganic fillers totally changes the way the uncured materials flow. All the experimental composites show a strong non-Newtonian shear-thinning behavior. This

confirms the results found previously on commercially available formulations. Results for the complex viscosity versus frequency of the composites tested are shown in Figure 3-7.

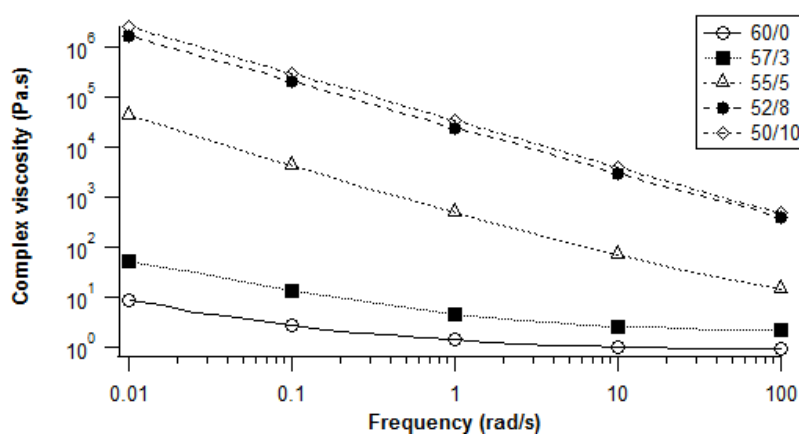


Figure 3-7: Complex viscosity (η^*) versus frequency of the experimental composites tested.

Although all the materials tested have the same total filler load by weight, their rheological behavior is drastically different from each other. Indeed, 60 % of macrofiller alone does not have a major influence on the viscoelastic properties, except that it increases the Newtonian viscosity and that a slight shear-thinning behavior appears. But the more the microfiller content increases, the more the complex viscosity increases. Indeed, at 1 rad/s, complex viscosity increases from 1.4 Pa.s for the composite with no microfiller to 34,000 Pa.s with 10 % microfiller. As a comparison, viscosity increases from 0.2 Pa.s for the unfilled Bis-GMA/TEGDMA 50/50 mixture to 1.4 Pa.s when 60 wt% macrofiller is added. Furthermore, the more the microfiller content increases, the more shear-thinning the materials becomes.

Regarding the results of the elastic moduli versus frequency that are presented in Figure 3-8, it can be concluded that as the microfiller increases, the elastic moduli increase while their slope decrease, with no hint of terminal behavior at the lowest frequencies. The slopes of G' for the 55/5, 52/8 and 50/10 materials can be approximated as a horizontal, which, in conjunction with the absence of Newtonian plateau for the complex viscosities at low frequencies, indicates high elasticity and a strong solid-like behavior at rest, i.e. they are yield stress materials and won't flow under their own weight.

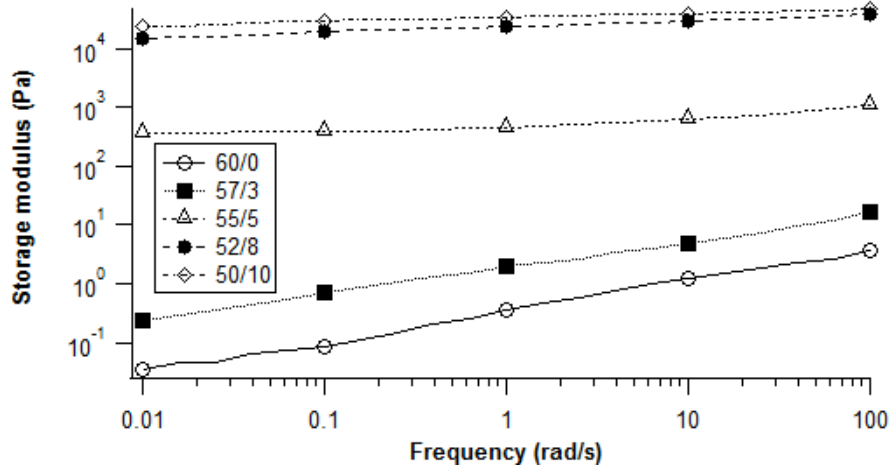


Figure 3-8: Storage modulus (G') versus frequency of the experimental composites tested.

These elements lead to the conclusion that the microfiller is the major determinant of the final rheological properties of resin composites. As its content increases, complex viscosity increases drastically, shear-thinning behavior increases, elasticity increases and solid-like behavior at rest appears. This is confirmed by the fact that the strain limit of the linear viscosity range of the composites tested decreases dramatically as the microfiller content increases, from 20 % for the 60/0 sample to 0.1 % for the 52/8 and the 50/10 samples. This is further indication of a growing internal structure of the materials as their microfiller content increases.

From the present observations it can be assumed that there is probably a specific point in the formulation of resin composites where rheological properties drastically change from mainly liquid-like to solid-like materials. This can be explained as the minimal content of microfillers required to create a gel structure. In the limitations of this study, this point lies around 5 % of microfillers, as shown in Figure 3-9 where the 55/5 sample stands at the beginning of the huge increase of the complex viscosity versus microfiller content at 1rad/s.

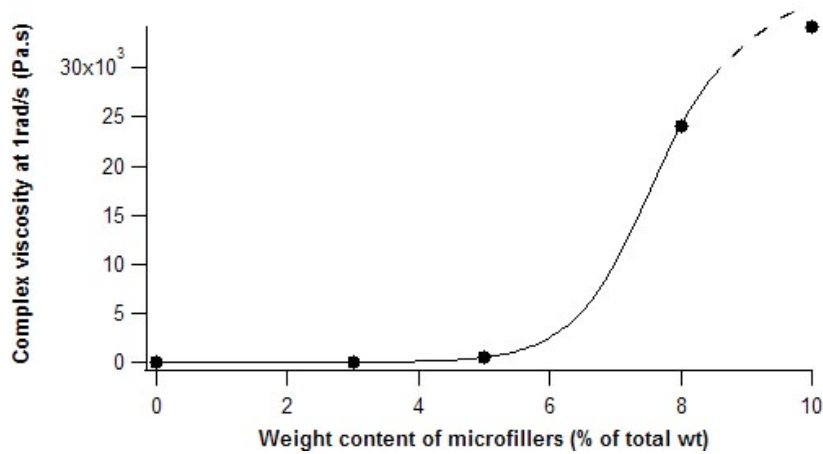


Figure 3-9: Complex viscosity at 1 rad/s versus weight content of microfillers of the experimental composites tested. The curve indicates the probable evolution of the viscosity.

Results of the evolution of the complex viscosity versus time after destructuring clearly show that the materials tested exhibit thixotropy, except for the 60/0 composite for which no noticeable variation of the viscosity through time could be observed. All the other samples' complex viscosities decrease dramatically to 0.3-0.6 times that of equilibrium state and take about 1 hour to reach 80 % of their initial viscosity and up to 4 hours to return to their state of equilibrium. This is shown in Figure 3-10.

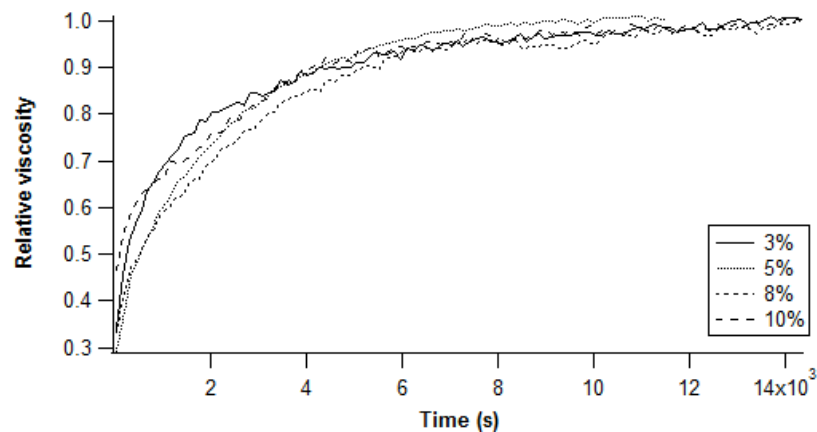


Figure 3-10: Relative viscosity of the experimental composites as a function of time after deformation (the 1 value is the viscosity of the sample without any prior deformation).

As for the commercially available resin composites, the return to equilibrium can be analyzed and a time constant can be extracted. Whatever the macrofiller/microfiller ratio, the time constant for each material remains globally the same, as shown in Table 3-2. As a consequence, their curves are pretty much parallel to each other (Figure 3-11).

Material	Complex viscosity (Pa.s) at 0.1 rad/s		Time constant (s)
	t = 0 s	t = 14,400 s	τ (Chi ²)
60/0	2.4289	3.8284	N/A
57/3	17.516	51.502	2463.96 (0.05)
55/5	2058.3	7052.4	2190.7 (0.01)
52/8	31241	93432	2970.34 (0.02)
50/10	83196	177970	2893.64 (0.02)

Table 3-2: Complex viscosity (η^*) as a function of time after deformation. The right column shows the time constant of the return to equilibrium.

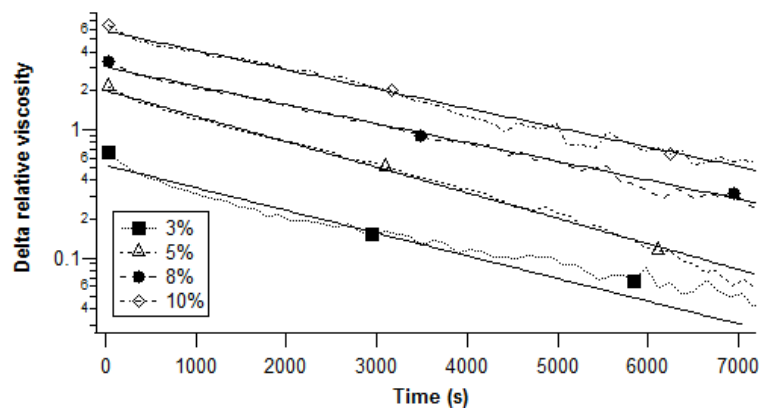


Figure 3-11: Analysis of the return to equilibrium of the experimental composites as a function of time after deformation. Values of the 55/5, 52/8 and 50/10 samples are shifted by a factor 3, 4 and 10, respectively.

The first hypothesis that was made in order to explain thixotropy of resin composites was that the internal structure, from a rheological point of view, is linked to the spatial organization of the microfiller. Indeed, as the complex rheological properties seem dictated by the amount of microfiller and as microparticles are only partially silanized, it was assumed that the decrease of the viscosity was the consequence of the destruction of a tri-dimensional network of microparticles formerly linked together via hydrogen bond and that recovery of the initial viscosity was the sign of the secondary reconstruction of the network. However, TEM microphotographs that were performed on destructured and non-destructured sample did not show any difference in the dispersion of the microfiller. There is thus no visible destruction and recovery of a microfiller network (Figure 3-12).

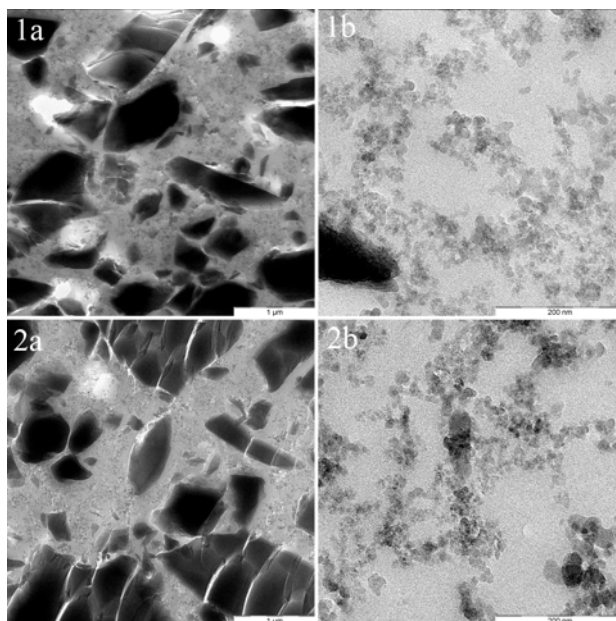


Figure 3-12: Dispersion of the fillers by transmission electron microscopy immediately after complete destructure at 5000 x (1a) and 40,000 x (1b) magnifications and without any destructure at 5000 x (2a) and 40,000 x (2b) magnifications.

The alternative explanation is that due to the large contact area generated by the microfiller, a very important part of the monomer interacts with the fillers surface. From then, interaction may result in a layer that surrounds the particles where monomers' mobility is restricted, resulting in a significant local increase of the viscosity. This has already been demonstrated in dispersion of silica in rubbers where the thickness of this layer is linked to both the specific surface of the particles and the nature and amount of surface treatment [15, 16].

While complex viscosity and elastic modulus are strongly influenced by the amount of microfiller, thixotropy does not depend on the microfiller load, but only on the presence or absence of microparticles. Further studies are needed to investigate the exact nature of the interactions that exist between both the filler particles and between the filler particles and the organic matrix. Indeed, while the theory of low-mobility monomers surrounding the particles may explain the evolution of the complex viscosity and elastic moduli as the microfiller content increases by the progressive disappearance of the regions where monomers can move freely, it is not sufficient to totally explain the time dependence of the viscosity after deformation. Particles interactions with the organic matrix must be investigated, of course, but as resin composites are highly filled, the study of particle-particle interactions is of upmost importance and is probably more likely to explain thixotropy. Indeed, in highly filled

suspensions, also called nondilute suspensions because the amount of filler makes particle-particle interactions unavoidable, rheological properties are by the way strongly dictated by the way each particle acts on the behavior of those surrounding it. Mechanisms are numerous and complex: dispersion forces (i.e. London-Van der Waals), electrostatic forces, steric forces and even hydrodynamic interaction forces by alteration of the streamlines that surround the particles must be considered. For materials that are highly structured, it has been described that at relatively low stress levels, most of the rest structure persists and the response is either elastic or viscoelastic. In any case, the viscosity reaches extremely high levels. Then the mechanism of motion is creep rather than flow, meaning that a particle network exists at all times and that motion is based on subsequent local rearrangements of the structure [10]. But local rearrangements require a finite amount of time, resulting in time-dependant viscosities such as those observed in resin composites.

3. Clinical implications of the rheological behavior of resin composites (Chap. 7 & 8)

Although the study of the rheological properties of resin composites is conducted *in vitro* and require experiments that are far from the different steps of their clinical handling, links to clinical implications are quite obvious since the composite restorations techniques lay mainly in the controlled flow and deformation of the material in a tooth cavity. Within the limitations of this work, two clinical implications may be easily investigated. On one hand, since commercially available materials, although belonging to the same classification, present rheological behaviors that are very different from one to another, is it possible to further classify them according to possible clinical indications based upon their flow properties? On the other hand, since they all show thixotropy and since it has been demonstrated that their return to equilibrium takes several hours, resin composites are polymerized clinically in a state that is far from internal equilibrium. As thixotropy is probably mainly due to rearrangements in the structure of the materials, what happens to their mechanical properties when they are cured just after severe deformation as it is the case clinically?

3.1. Physical, mechanical and rheological characterization of resin-based pit and fissure sealants compared to flowable resin composites (Chap. 7)

The caries preventive action of resin-based pit and fissure sealants rely on the establishment of an effective mechanical obstacle to the leakage of nutrients to cariogenic microorganisms in the deeper part of fissures [17, 18, 19]. In addition, unlike glass ionomer

sealants that release fluoride in the surrounding enamel, there is no remnant action of the material once it has disappeared. The success of a resin-based sealant depends thus on two factors: the establishment of a hermetic seal of fissures and the long-term retention of the material.

It is thus of major importance that materials used as pit and fissure sealants may flow properly in the deepest parts of pits and fissure in order to provide effective seal. Moreover, as preventive pit and fissure sealants are not or poorly exposed to occlusal stresses, invasive sealants are more likely to undergo mechanical solicitations. In this particular situation, the mechanical properties of the material that is used will play an important role in the long-term success of the procedure.

In addition to specifically designed resin-based pit and fissure sealants, many flowable resin composites are claimed by their manufacturers to be suited for pit and fissure sealing. The purpose of this study was to compare the rheological and mechanical properties of traditional resin-based pit and fissure sealants and flowable resin composites in order to determine their ability to efficiently seal pits and fissures and to resist over time.

As it was expected, the mechanical properties of pit and fissure sealants are dramatically lower than those of flowable resin composites which filler loads are by far higher than those of pit and fissure sealants. But as stated above, it is probably of minor importance in the case of preventive pit and fissure sealing since the pits and fissures of occlusal surfaces do not encounter much stresses during clenching, as it was shown by Dejak et al. [20]. In that case, a good resistance to wear is certainly more important than high elastic moduli. This can indirectly be evaluated by microhardness tests. The results of Vickers microhardness show that flowable resin composites have higher hardness than pit and fissure sealants and that among flowable composite, those which exhibit the highest values are those which contain nanofillers.

In the case of enlarged pit and fissure sealing, mechanical properties are to be taken into account. It is clear that flowable resin composites' elastic moduli are much higher than those of pit and fissure sealants. As for the microhardness results, the materials that show the highest dynamic and static moduli of elasticity are nanofilled or nanohybrids.

As expected according to rheological measurements previously performed on both types of materials (Chap. 5), all the materials tested in this study show complex rheological properties and particularly shear-thinning. Pit and fissure sealants, although they are very low viscosity materials, exhibit signs of elastic behavior at low frequencies but it can be assumed that their internal structure is not strong enough to counteract gravity and, by the way, to

induce a solid-like behavior at rest and prevent creep flow. For the flowable resin composites, two groups were distinguished within the limitations of the study. The first one has higher viscosities and storage moduli than the others. In addition, the slope of their storage moduli indicates a very strong elasticity and thus a very strong solid-like behavior at rest. The second group shows materials that have a lower viscosity and storage moduli with higher slopes at low frequencies, which is an indication of a weaker internal structure and less solid-like behavior at rest. In a previous study, a third group was made that was in between the others and that presented lower viscosity by storage moduli close to the horizontal at rest, indicating lower viscosity but strong solid-like behavior anyway.

Clinically, it means that a material that belongs to the second group is more likely to flow by itself in small cavities and fissures than the other resin composites tested, which, in the particular case of pit and fissure sealing, can lead to a better application of the material.

As a conclusion and from the results found in this study, since preventive pit and fissure sealing does not seem to require materials with high mechanical properties, the use of materials that are specifically designed for that purpose look totally adequate. But if pits and fissures need to be enlarged, materials with higher mechanical properties are required and, so far, flowable resin composites are much better than pit and fissure sealants. The term “flowable” is unfortunately vague. For this specific clinical condition, a material with a low elastic behavior at low frequencies is required for its ability to flow into small areas.

It is however to be noted that the rheological properties of the material that is used are not the sole factors that rule the quality of the sealing. Of course, the surface tension after etching but also the adhesive system that is use in conjunction with flowable resin composites may influence positively or negatively the quality of the sealing.

3.2. Mechanical properties of experimental and commercially available resin composites as a function of time between handling and curing (Chap. 8)

The mechanical resin composite are measured *in vitro* in optimal conditions. It is however well known that they may vary according to many factors. Some of them are obvious: the amount of filler particles, the particle size and silanation [21, 22, 23] or the quality of the organic matrix and especially the degree of conversion and the crosslink density [24, 25, 26]. But only very poor information is available on the possible influence of the handlings procedures themselves.

As it was shown in the previous studies of the present work, resin composites show thixotropy. This property is linked to a strong internal structure that most probably encounters

local rearrangements when materials are submitted to flow. These rearrangements take time to reach a new equilibrium [10]. As developed previously, resin composites are thus, when used in clinical conditions, polymerized in a state of internal structure that is disturbed since they are cured immediately after deformation. Since rearrangements have a huge influence on the viscosity of resin composites, the question can be legitimately asked if they also have an influence on other properties and especially on the mechanical properties.

In the present study, the dynamic moduli of elasticity of both an experimental and commercially available formulations were investigated as a function of time after deformation. To this end, different samples of each material were prepared with the peculiarity of respecting different times of rest between deformation and polymerization. In addition, the spatial organization and morphology of the inorganic fraction was evaluated using transmission electron microscopy.

For the experimental resin composite tested, which formulation is the same as the 55/5 sample used in the study of the rheological properties of experimental composites (Chap. 6), a significant increase of its dynamic modulus as a function of time was observed. The same observation was made for several commercially available materials. As an example, values for the Admira Flow are presented in Figure 3-13.

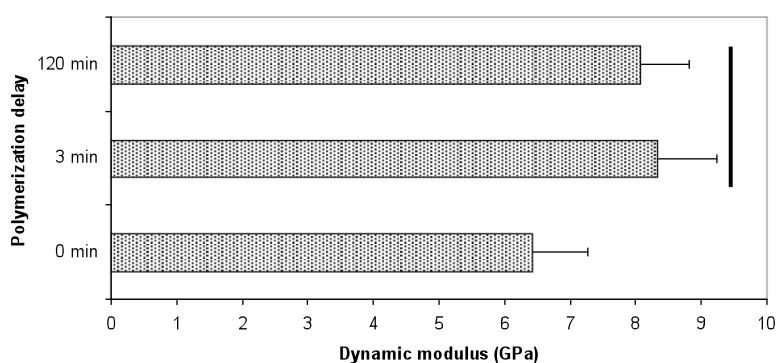


Figure 3-13: Dynamic moduli of elasticity according to the delay between handling and curing for the Admira Flow. Groups that are not statistically significant ($p < 0.05$) are connected by the vertical bar.

Although values are not statistically significant for all the groups, there is an indisputable increase of the dynamic modulus of elasticity over time. However, all the materials tested did not exhibit such an evolution, as Filtek Supreme XT Flow, which values are presented in Figure 3-14.

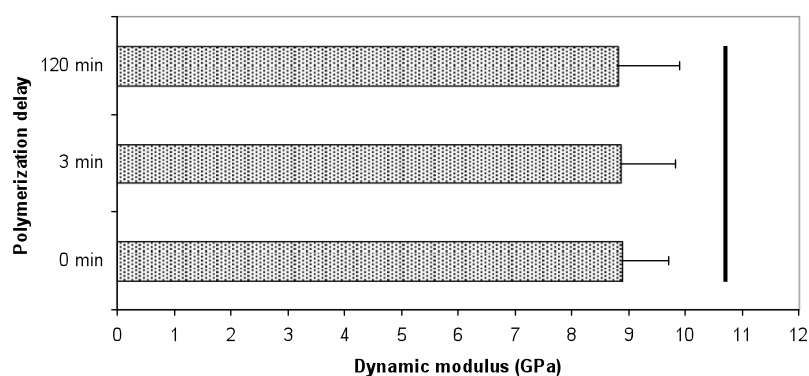


Figure 3-14: Dynamic moduli of elasticity according to the delay between handling and curing for the Filtek Supreme XT Flow. The vertical bar connects groups that are not statistically significant ($p < 0.05$).

Although no correlation could be made between the presence or absence of significant evolution of the dynamic moduli over time and the filler load in weight, interesting observations were made regarding the types and dispersion of filler particles in the organic matrix. Indeed, all the materials that contain fumed silica aggregates, i.e. all the microhybrids, theOrmocer and the experimental resin composite tested, show a significant increase of their elastic moduli over time after deformation. What only changes from one material to another is the amplitude of the increase of the dynamic modulus and its statistical pattern. The first group, just after handling, is different from all the others; the last group (the one for which viscosity has reached equilibrium again) is different from the first ones. Materials for which no significant variation of the dynamic moduli over time could be observed all contain isolated nanofiller. Examples of the different types of morphology and dispersion of the inorganic fraction from one material to another is shown in Figure 3-15.

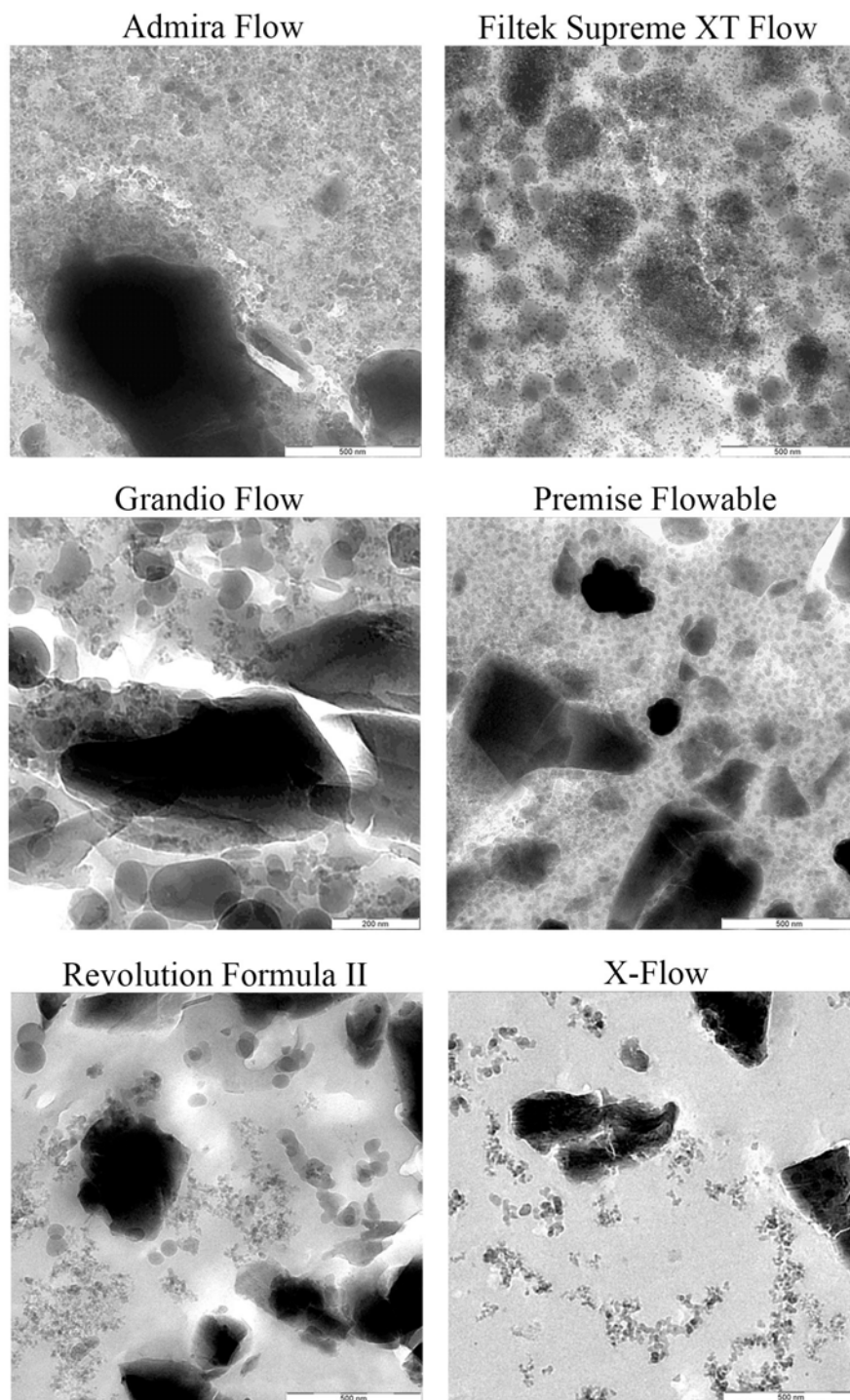


Figure 3-15: Dispersion of the fillers by transmission electron microscopy at 12,500 x magnification, except for Grandio Flow which is at 20,000 x magnification for clarity purpose.

Not surprisingly, no correlations could be made between the macrofiller and the variation of the dynamic moduli over time. Indeed, as the macrofiller has a huge positive influence on the final mechanical properties as well as on the polymerization shrinkage of resin composites, it has only very minor influence on their rheological properties: the

Newtonian viscosity is increased but only a very slight shear-thinning behavior appears and no time-dependence of the rheological behavior (i.e. thixotropy) may be observed.

The fact that nanofiller-containing composites did not show a significant variation of their dynamic moduli over time may be probably partially explained by the fact that nanoparticles present reduced interactions due to optimal silanation. It was developed previously that thixotropic materials are subjected to local rearrangements in their internal structure after deformation. Nanofiller-containing materials maybe present a weaker internal structure than those which contain fumed silica aggregates and, as a consequence less modifications in their internal structure when submitted to flow with the results of more stable properties. However, the nanofiller-containing materials that were tested in the field of this work showed thixotropy anyway. The evolution of the dynamic moduli of elasticity over time of some materials can thus not be only explained by their thixotropic behavior. Nevertheless, it is probably more the type of filler that influences their variation than the amount of it, as it is more the type of filler that influences the thixotropic behavior than the amount of it.

4. General conclusions

Resin composites have proven to be rheologically complex materials. From the rheologist's point of view, the complex properties that highly filled suspensions show, particularly yield stress and thixotropy, are not yet fully understood and as they are still a matter of debate, they are still nowadays an active area of research [10]. Applied to resin composites, this work brings basic understanding on the rheological properties of composites as well as elements on the influence of each component on final viscoelastic properties. It is understood that some complex rheological properties such as shear-thinning are influenced by the type and amount of filler particles while other properties, such as thixotropy, seem to only depend on the type of filler but not on its amount. Although the real mechanisms that rule these properties are still unknown, it can reasonably be assumed that they are not simple particle-particle interactions. Hence, as interactions that filler particles with their surrounding environment may be of many types (electrostatic forces, hydrodynamic interactions, steric forces etc.), it can be supposed that the relative importance of each type of interaction exerts a different influence on the flow behavior of the material. In this context, the thorough comprehension of what really happens is a huge and complicated challenge.

However, it is not necessary to get our knowledge to that point in order to better control the rheological properties of resin composites. A basic measurement of the effect of

the ratio of various types of fillers, such as done in this work, already allows formulating materials for which viscoelastic properties are not a consequence of trials and errors anymore.

Although rheological studies of composites are still marginal nowadays, the clinical interest of specific viscoelastic properties is obvious as according to particular clinical situations, practitioners need materials with specific flow behaviors. And, as it was discussed thoroughly above, a specific flow behavior is not just a specific viscosity (flowable, universal or packable): it is the reunion of a specific viscosity, particular viscoelastic characteristics, a shear rate or frequency of deformation and last but not least, a history of the previous deformations the material encountered as its rheological properties are time-dependent. The sum of all these conditions dictates the particular flow characteristics of the material that is used at a particular moment in a particular situation. And as it was shown, composites that belong to the same category of viscosity as claimed by manufacturers may exhibit totally different clinical behaviors.

Furthermore, it was shown that as well as rheology is handling time-dependent, other properties such as mechanical properties may be time-dependent as well. Although the variations of the mechanical properties cannot be explained by the mechanisms that rule the time-dependence of the rheological properties, both phenomena are most certainly intimately linked.

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4. CHARACTERIZATION OF NANOFILLED COMPARED TO UNIVERSAL AND MICROFILLED COMPOSITES

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ABSTRACT

Objectives: The purpose of this study was to compare the inorganic fraction and the mechanical properties of three nanofilled composites with four universal hybrid and two microfilled composites. The degrees of conversion of the materials photopolymerized using halogen and LED units were also investigated.

Methods: Three nanofilled (Supreme, Grandio and Grandio Flow), four universal hybrid (Point 4, Tetric Ceram, Venus, Z 100) and two microfilled (A 110, Durafill VS) composites were used in this study. Their filler weight content was measured by thermogravimetric analysis. The morphology of the filler particles was determined using scanning-electron microscopy (SEM). Mechanical properties were measured: dynamic and static elastic moduli, flexural strength and Vickers microhardness. The degree of conversion in relation with the depth of polymerization of every material tested was evaluated using Raman spectrophotometry.

Results: Nanofilled resin composites show higher elastic moduli than those of universal and microfilled composites, except for the Z-100. The microfilled composites exhibit by far the lowest mechanical properties. The flexural strength does not appear as a discriminating factor in this study. The degrees of polymerization obtained with the halogen lamp are higher than those obtained with the LED lamp.

Significance: Nanofilled resin composites show mechanical properties at least as good as those of universal hybrids and could thus be used for the same clinical indications as well as for anterior restorations due to their high aesthetic properties.

KEYWORDS

Resin composites, nanofillers, filler morphology, mechanical properties, polymerization

1. Introduction

Since the very first dental resin composites were developed, many efforts to improve their clinical performance have been undertaken [1]. Research on the resin matrix is mainly based on the development of new monomers [2, 3, 4, 5] while studies on the filler content focus on loading, particle size, silanation [6] and on the development of new particles [7, 8]. Such studies are of high importance because the mechanical properties of dental composites depend highly on the concentration and particle size of the filler. The compressive strength, hardness, flexural strength and elastic modulus increase with the amount of inorganic fraction while the polymerization shrinkage is said to decrease [6].

One of the most important advances of the last few years in this field is the application of nanotechnology to resin composites. Nanotechnology is known as the production and manipulation of materials and structures in the range of about 0.1 to 100 nanometers by various physical or chemical methods [9]. While the size of the filler particles lies around 8-30 μm in hybrid composites and 0.7-3.6 μm in microhybrid composites [10], recently, new fillers with size ranging from around 5 to 100 nanometers have been developed [11] although 40 nm particles were already present in microfilled composites. These materials could thus be considered as precursors of nanofilled composites.

The use of nanoparticles is useful for many applications including industry, transport, packaging, high performance coatings, electronics, biomedical, where nanoparticles improve mechanical properties of materials. In dentistry, posterior class I or II restorations require composites that show high mechanical properties while anterior restorations need composites that have superior aesthetics. The resin composite that meets all the requirements of both posterior and anterior restorations has not emerged yet.

Therefore, nanotechnology is of great interest in resin composite research. Due to the reduced dimension of the particles and to a wide size distribution, an increased filler load can be achieved with the consequence of reducing the polymerization shrinkage [1] and increasing the mechanical properties such as tensile strength, compressive strength and resistance to fracture. These seem to be equivalent or even sometimes higher than those of universal composites and significantly higher than those of microfilled composites [1, 11, 12]. On the other hand, the small size of the filler particles improve the optical properties of resin composites because their diameter is a fraction of the wavelength of visible light (0.4-0.8 μm), resulting in the human's eye inability to detect the particles [12]. Furthermore, the wear

rate is diminished and the gloss retention is better [12, 13]. As a consequence, manufacturers now recommend the use of nanocomposites for both anterior and posterior restorations.

The objective of the present study was to characterize the inorganic fraction and to measure the mechanical properties and the degree of conversion of three commercially available nanofilled composites compared to four universal and two microfilled composites. The inorganic fraction was characterized by scanning-electron microscopy (SEM) and by thermogravimetric analysis (TGA). The mechanical properties measured were dynamic and static moduli of elasticity, flexural strength and Vickers microhardness. The degree of conversion was evaluated by Raman spectrophotometry.

2. Materials and methods

2.1. Resin composites

Nine commercial resin composites (two microfilled, three nanohybrids and four universal) were tested in this study. They are listed in Table 1.

Material	Manufacturer	Type	Shade	Batch
A110	3M-ESPE (St Paul, MN, USA)	Microfilled	A3	20030523
Durafill VS	Heraeus-Kulzer (Wehrheim, Germany)	Microfilled	A2	090140
Supreme	3M-ESPE (St Paul, MN, USA)	Nanofilled	A3	3BN
Grandio	Voco (Cuxhaven, Germany)	Nanofilled	A3	371474
Grandio Flow	Voco (Cuxhaven, Germany)	Nanofilled	A3	450086
Point-4	Kerr (Orange, CA, USA)	Universal	A3	306357
Tetric-Ceram	Ivoclar-Vivadent (Schaan, Liechtenstein)	Universal	A3	F36861
Venus	Heraeus-Kulzer (Wehrheim, Germany)	Universal	A2	190030
Z-100	3M-ESPE (St Paul, MN, USA)	Universal	A3	3WX

Table 4-1: List of materials tested.

2.2. Percentage and morphology of inorganic fraction

2.2.1. Weight percentage of fillers

The weight percentage of fillers was determined using Thermogravimetric Analysis (TGA/SDTA861^e, Mettler-Toledo, Greinfensee, Switzerland). It evaluated weight changes as a function of time and temperature during a thermal program ranging from 30°C to 900°C at the rate of 10°C/min in normal atmosphere followed by air cooling to room temperature. The calculated ratio between the final weight of the sample and its nominal weight is assigned to the inorganic fraction. Three samples of each material were analyzed.

2.2.2. Fillers morphology

The fillers morphology was determined using SEM. Unpolymerized monomers were removed by a washing technique: 0.5 g of each material was dissolved in 4 ml of acetone and centrifuged for 5 min at 700 g. This process was repeated three times using acetone and three others with chloroform for a further washing and to ensure a complete elimination of the unpolymerized resin. The remaining fillers - including prepolymerized fillers - were suspended in 2.5 ml of absolute ethanol, smeared on a glass slide (7.5 x 2.5 cm) and dried at 37°C during 6 hours. After gold-coating, fillers were observed by SEM (Leica Stereoscan S-260, Cambridge, UK) at 5,000 and 10,000 magnifications.

2.3. Mechanical properties

Five specimens of each material were prepared in moulds of 25 x 2 x 2 mm as specified in the ISO specification 4049. Samples were light-cured using two conventional curing devices (XL 3000, 3M-ESPE, St Paul, MN, USA, 650 mw/cm²) by overlapping irradiations for a total of 60 s on both sides. The same specimen was used to measure the following properties: dynamic modulus, static modulus and flexural strength, Vickers microhardness. Specimens were stored for 7 days in water at 37°C before measurement.

2.3.1. Dynamic modulus

The dynamic modulus of elasticity was measured non-destructively by the impulse excitation technique (Braem *et al.*, 1986) [14]. Each sample was set in flexural vibration by a light mechanical impulse. The signal produced was captured via a microphone placed underneath the sample by a special signal analyzer, the Grindosonic (Lemmens Elektronics, Haasrode, Belgium). Modulus of elasticity (GPa) was calculated from the fundamental frequency, the mass, the width, the length and the thickness of the bar as follows:

$$E_d = 0.9465 \frac{mf_t^2}{b} \frac{L^3}{t^3} T_1$$

where m is the mass of the bar, b the width of the bar, L the length of the bar, t the thickness of the bar, f_t the fundamental frequency of the bar in flexion – which appears on the screen of the machine -, and T_1 a correction factor for fundamental flexural mode to account for finite thickness of the bar, Poisson's ratio and other constants. Poisson's ratio is the ratio of transverse strain (contraction) to axial strain (elongation) in a uniaxial tensile test [15]. When applied to dental resin composites, its value lies around 0.30 [16], which value has been taken as the mean value for all the materials tested in this study.

2.3.2. Static modulus and flexural strength

The static modulus was measured using a three-point bending setup according to the ISO-4049 specification [17]. Samples were loaded in an Instron machine (Instron 5566, High Wycombe, UK) at a speed rate of 0.75 mm/min until fracture occurred. The load and the corresponding deflection were recorded and used to calculate the modulus (GPa) and the strength (MPa):

$$E_s = \frac{Fl^3}{4bh^3d}$$

where F is the load, l the distance between the supports, b the width of the bar, h the thickness of the bar and d the deflection corresponding to the load F.

The flexural strength was calculated as follows:

$$\delta = \frac{3Fl}{2bh^2}$$

where F is the maximum load at the point of fracture, l the distance between the supports, b the width of the sample and h its height.

2.3.3. Vickers microhardness

Microhardness measurements were carried out on the fractured samples issued from the previous test with a Durimet microhardness tester (Leitz, Wetzlar, Germany). A load of 200 g was applied during 30 s on their surface. The length of the diagonal of each indentation was measured directly using a graduated eye-lens. The Vickers Hardness Number is obtained using the following equation:

$$H = \frac{1854.4 \times P}{d^2}$$

where H is Vickers hardness in kg/mm², P the load in grams and d the length of the diagonals in μm [18].

2.4. Photopolymerization sensitivity

Specimens were prepared by placing each material in a 6 mm depth tin mold and by light-curing it at the surface of the mold. The composites were polymerized with the XL 3000 (3M-ESPE, St Paul, MN, USA) during 40 seconds (with an intensity of 650 mW/cm²) and with the Elipar Freelight 2 (3M-ESPE, St Paul, MN, USA) during 10 seconds (with an intensity of 450 mW/cm²) as recommended by the manufacturer.

The degree of conversion (DC) of 6 mm thick samples was measured from the top surface (the one in contact with the tip of the light source) to the bottom with 0.5 mm steps. DC was evaluated with a Raman spectrophotometer (Labram, Dilor, Lille, France) according to the technique described by Pianelli et al. in 1999 [19]. Samples were excited at 632.8 nm by He-Ne laser through a microscope objective (X100). Spectra were obtained in the region of 2000 to 1100 cm^{-1} after five accumulations of 60 s using a confocal hole of 200 corresponding to an approximate volume of 6 μm^3 . It allows the evaluation of the degree of conversion i.e. the percentage of vinyl functions converted to aliphatic functions, by comparing the vibration band of the residual unpolymerized methacrylate C=C bond at 1640 cm^{-1} with the aromatic C=C stretching band at 1610 cm^{-1} used as an internal standard. The DC of the selected composite resins was calculated as follows:

$$DC\% = 100 \left[1 - \frac{R_{\text{polymerized}}}{R_{\text{unpolymerized}}} \right]$$

where R is the ratio between peak heights at 1640 cm^{-1} and at 1610 cm^{-1} .

2.5. Statistical analysis

Statistical analysis for all the mechanical properties was made using a one-way ANOVA and post-hoc Scheffe's tests at $p < 0.05$ level. This was performed separately for each of the different mechanical properties.

3. Results

3.1. Percentage and morphology of inorganic fraction

The mean values and standard deviations of the percentage of fillers by weight are shown in Figure 1. They ranged from 51.3 % for the Durafill VS to 84.1 % for the Grandio. For the universal hybrid composites, values varied between 71.0 % and 79.7%, for the microfilled composites between 51.3 % and 54.9 % and for the nanofilled composites between 71.9 % and 84.1 %.

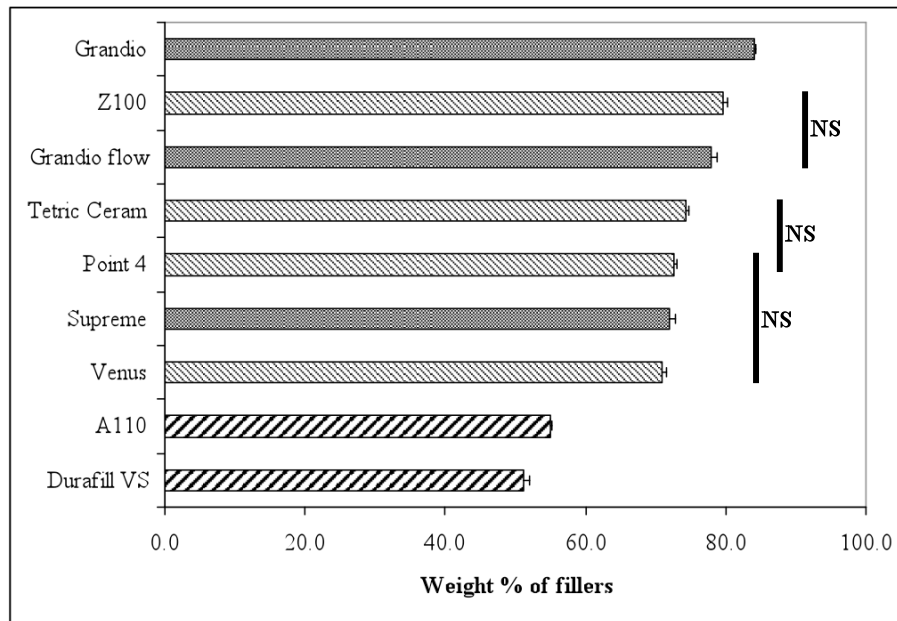


Figure 4-1: Mean values and standard deviations of the percentage of filler by weight of the composites determined by thermogravimetric analysis. Vertical bars connect values that are not statistically significant ($p < 0.05$).

The SEM microphotographs are shown in Figure 2. Images in the boxes are twice the enlargement of the big ones. Z-100, Supreme and Point-4 showed spherical particles. Irregular shaped particles were found in Grandio, Grandio Flow, Tetric-Ceram and Venus. Microfilled composites contain large filler aggregates.

3.2. Mechanical properties

Mean values and standard deviations of the dynamic moduli of elasticity of the materials tested are shown in Figure 3. Values varied between 6.3 GPa for the Durafill VS to 26.3 GPa for the Grandio.

Values for the static moduli of elasticity are shown in figure 4. They ranged from 2.6 GPa for the Durafill VS to 14.2 GPa for the Grandio.

For the flexural strength, results are shown in Figure 5. Mean values varied from 50.5 MPa for the Durafill VS to 123.4 for the Z-100.

The results for Vickers microhardness ranged from 18.9 (Durafill VS) to 102.6 (Z-100). Mean values and standard deviations are shown in Figure 6.

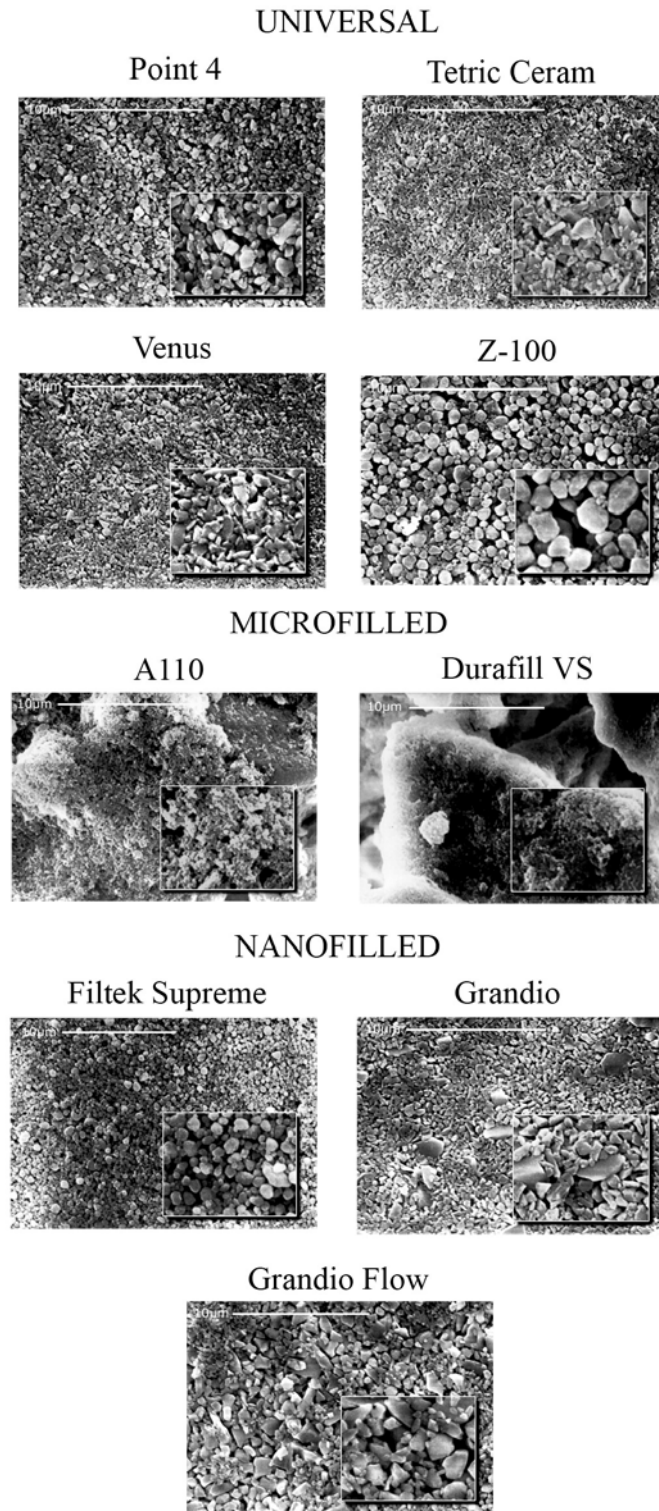


Figure 4-2: Fillers by scanning-electron microscopy at 5000x magnification (10000x in the box).

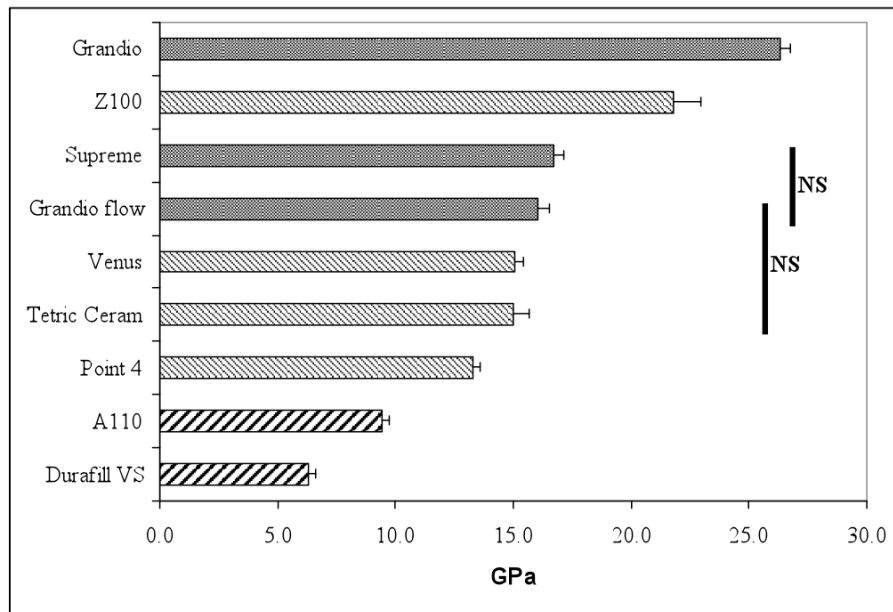


Figure 4-3: Dynamic moduli of elasticity of the materials tested. Materials that are not statistically significant ($p < 0.05$) are connected by vertical bars.

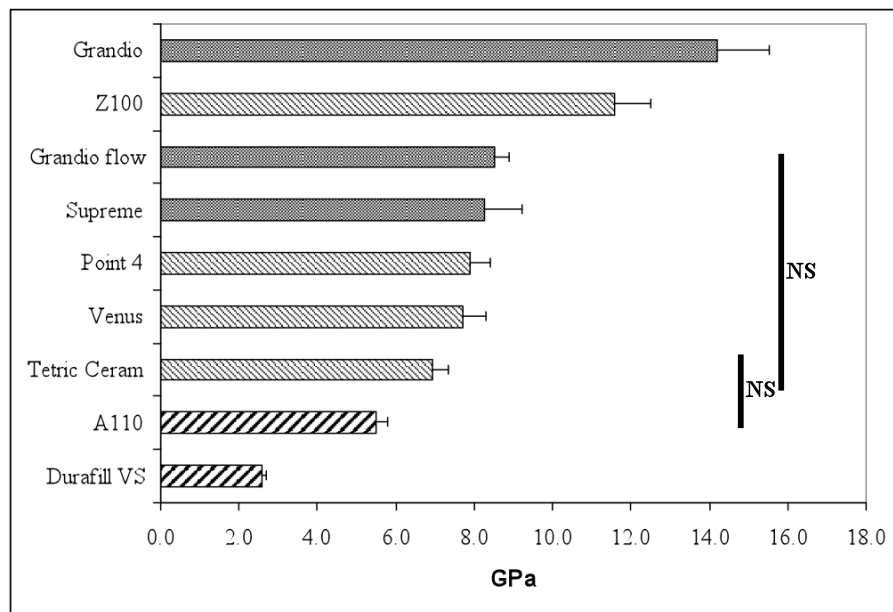


Figure 4-4: Static moduli of elasticity of the materials tested. Vertical bars connect materials that are not statistically significant ($p < 0.05$).

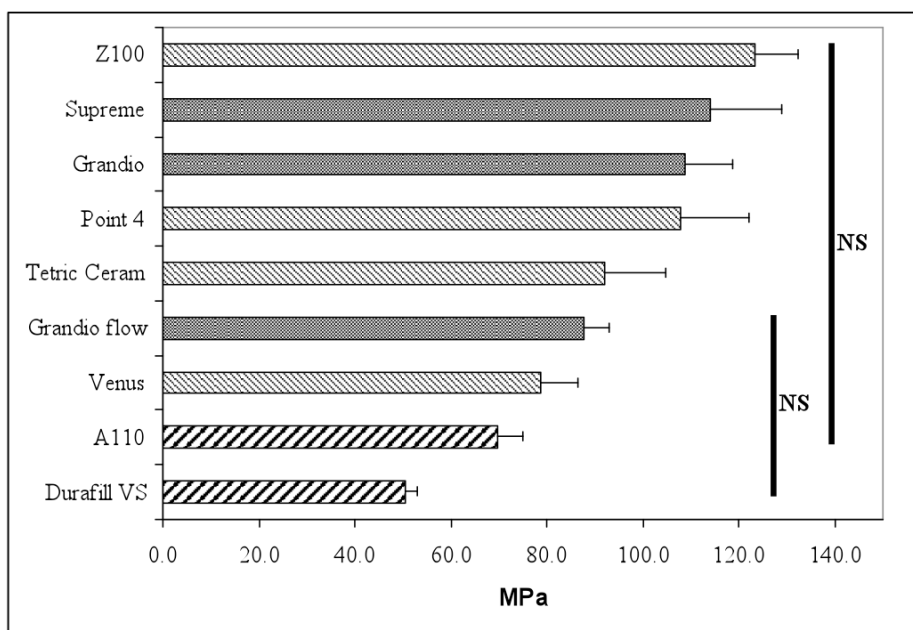


Figure 4-5: Flexural strength of the materials tested. Materials that are not statistically significant ($p < 0.05$) are connected by vertical bars.

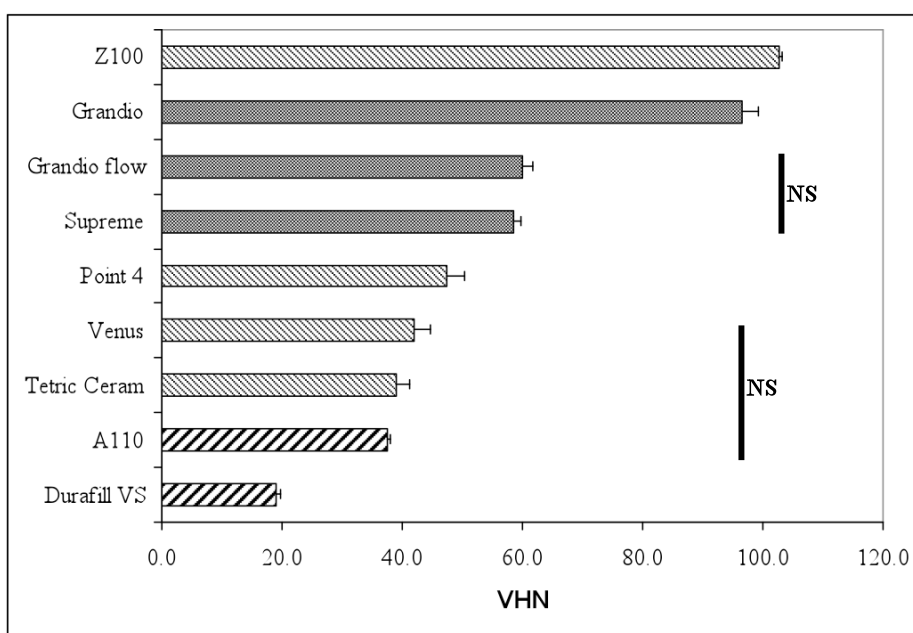


Figure 4-6: Vickers microhardness of the materials tested. Vertical bars connect materials that are not statistically significant at $p < 0.05$.

3.3. Photopolymerization sensitivity

The degrees of conversion of all the materials tested in relation with the depth in the sample irradiated with the XL 3000 are listed in Table 2. Table 3 lists the results obtained with the Freelight 2.

Thickness (μm)	Degree of conversion (%)				
	0	1000	2000	3000	4000
A110	56.50 (6.46)	48.91 (3.32)	49.42 (10.72)	41.39 (17.41)	10.59 (7.11)
Durafill VS	39.43 (7.09)	44.11 (1.71)	36.63 (11.72)	38.79 (3.12)	35.38 (1.28)
Supreme	45.39 (2.08)	47.92 (2.25)	42.82 (0.88)	37.20 (1.58)	28.01 (3.56)
Grandio	50.83 (3.27)	52.07 (1.47)	49.18 (1.64)	46.92 (3.82)	37.39 (4.95)
Grandio Flow	54.70 (2.65)	52.15 (1.05)	50.64 (0.16)	43.50 (1.58)	32.85 (3.60)
Point-4	62.25 (0.50)	61.29 (1.36)	59.40 (3.82)	51.80 (2.29)	40.52 (1.66)
Tetric-Ceram	47.42 (5.79)	55.38 (4.13)	53.06 (1.19)	46.58 (3.08)	43.55 (3.16)
Venus	49.81 (0.65)	50.49 (0.47)	49.51 (1.71)	44.18 (1.98)	34.93 (3.88)
Z100	50.43 (5.40)	51.77 (5.36)	49.07 (5.98)	43.42 (5.34)	33.33 (7.73)

Table 4-2: Degrees of conversion of all the materials irradiated with the XL-3000.

Thickness (μm)	Degree of conversion (%)				
	0	1000	2000	3000	4000
A110	49.83 (5.26)	35.92 (6.69)	24.94 (3.01)	5.41 (4.86)	0.00 (0.00)
Durafill VS	39.65 (3.12)	38.06 (0.33)	25.08 (1.47)	19.71 (2.03)	10.42 (0.37)
Supreme	45.56 (6.60)	38.71 (5.36)	31.72 (4.49)	20.00 (4.89)	4.98 (0.89)
Grandio	46.70 (3.75)	44.96 (3.22)	40.02 (6.55)	30.04 (7.25)	13.45 (1.95)
Grandio Flow	37.64 (3.39)	29.84 (5.37)	25.50 (4.47)	16.62 (4.89)	1.17 (2.02)
Point-4	59.64 (1.19)	55.20 (1.57)	48.80 (6.65)	30.28 (3.41)	2.03 (3.09)
Tetric-Ceram	54.63 (1.04)	50.00 (2.61)	35.28 (7.33)	0.00 (0.00)	0.00 (0.00)
Venus	49.09 (2.39)	46.56 (2.10)	41.85 (2.21)	28.26 (4.88)	9.43 (2.92)
Z100	49.84 (2.49)	48.05 (1.50)	45.74 (4.32)	36.14 (1.83)	20.43 (2.98)

Table 4-3: Degrees of conversion of all the materials irradiated with the Freelight 2.

For illustration purpose, the degree of conversion in relation with the depth for the Grandio is illustrated in Figure 7 for both curing units. Figure 8 shows the degree of conversion of the Supreme as a function of the depth of curing for both curing units.

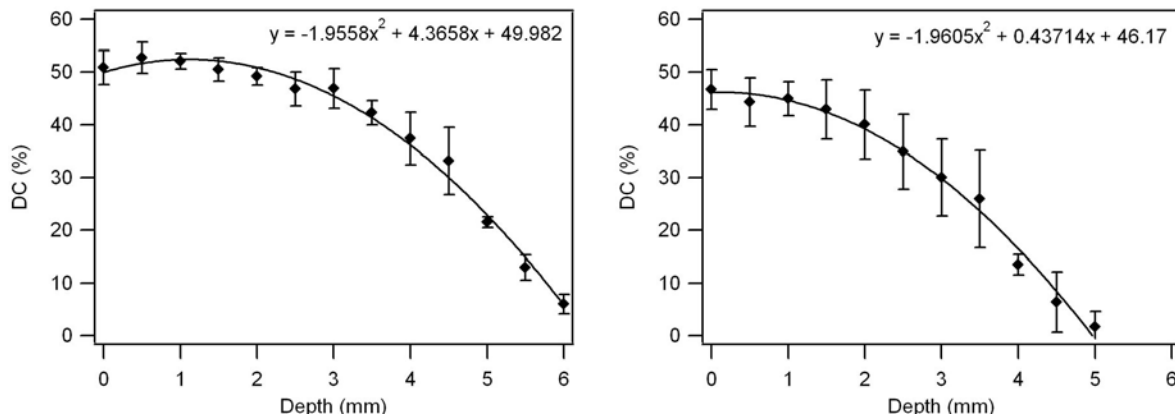


Figure 4-7: Degree of conversion obtained for the Grandio after 40 s of irradiation with the XL 3000 (on the left) and 10 s with the Elipar Freelight 2 (on the right).

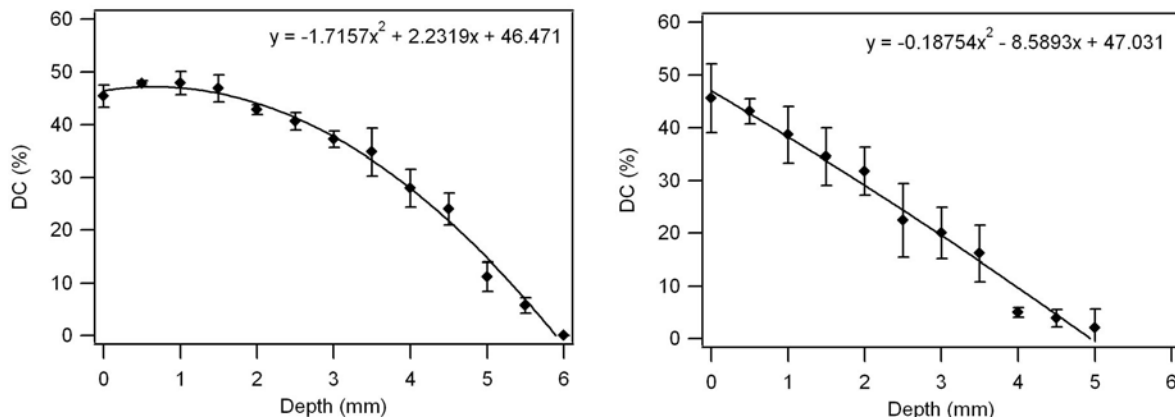


Figure 4-8: Degree of conversion obtained for the Supreme after 40 s of irradiation with the XL 3000 (on the left) and 10 s with the Elipar Freelight 2 (on the right).

4. Discussion

4.1. Filler load

The use of Thermogravimetric Analysis is a good method to determine the filler load in weight of dental resin composites, as demonstrated by Sabbagh *et al* [20] and the values obtained with this method are highly correlated to those obtained with the more traditional ashing in air technique. The nanofilled and universal composites exhibit almost the same range of percentages of fillers except for the Grandio, which filler load is significantly higher than the highest value obtained with the universal hybrids (Z-100). The percentages of fillers of the microfilled composites are significantly lower than those of all the other materials tested. Since increasing the filler content theoretically increases the viscosity, it is surprising to notice the percentage of the inorganic fraction measured for the Grandio Flow, which is nearly equivalent to that of the Z-100 and higher than those of other flowable composites as

found in the literature [20]. Manufacturers claim that including nanoparticles in resin composites allows the production of materials with an increased filler load and thus with better physical and mechanical properties without increasing their viscosity. Rheological studies should allow to confirm that nanofilled composites show viscosities and viscoelastic properties comparable to those of universal hybrid composites.

4.2. Filler shape

Most filler particles are of irregular shape. Spherical particles are found in Z-100, Point-4 and Supreme. A spherical shape is known to have many advantages such as to allow an increased filler load in composites [21] but also to enhance their fracture strength since mechanical stresses tend to concentrate on the angles and protuberances of the filler particles [22]. Irregular particles are found in Tetric Ceram, Venus, Grandio and Grandio Flow. Microfilled composites show large aggregates made of silica microfillers embedded in a prepolymerized organic matrix.

4.3. Mechanical properties

An optimal tooth restoration material should mimic structural, mechanical and physical characteristics of dentin and enamel [23]. Xu *et al.* [24] measured the elastic modulus of human enamel and dentin and obtained a mean value of 19 GPa for the dentin. Young's modulus of enamel was 94 GPa while depending significantly on tooth orientation. The mechanical properties of all the composites tested in this study are far from those of the enamel and lower than those of the dentin, which is in accordance with the results found by Sabbagh *et al.* in 2002 [23].

The Grandio and Z-100 exhibit significantly higher dynamic and static moduli of elasticity than all the other materials tested. The two other nanofilled composites (Supreme and Grandio Flow) are not significantly different but they have a significantly higher dynamic elastic modulus than the other hybrid composites. The microfilled composites (A 110 and Durafill VS) as well as the Point-4 have the lowest dynamic moduli. The static modulus of elasticity of the Supreme and the Grandio Flow are not significantly higher than those of the other universal composites. Again, the microfilled composites show the lowest values.

The measurement of the flexural strength was not a discriminating factor in this study. Indeed, all the composites, except the Durafill VS, show non significantly different values.

Z-100 shows the higher Vickers microhardness, directly followed by the Grandio. The other nanofilled composites show lower values, but still significantly higher than those measured for the other universal materials. The microfilled composites have the lowest microhardness.

The two composites that have the highest filler load (Z-100 and Grandio) show the highest mechanical properties: the nanofilled one has higher elastic moduli while the universal hybrid one has higher flexural strength and microhardness. The average filled composites have very close elastic moduli. The Supreme and the Point-4 have flexural strengths which are slightly lower than those of the Z-100 and the Grandio although they are not very highly filled. Since the Supreme and the Point-4 both contain spherical fillers, this could confirm the fact that composites containing spherical particles show higher flexural strengths [22].

The difference in the mechanical properties of the Grandio Flow compared to those of the Grandio is to be noticed. It is surprising because their filler loads are close from each other (respectively 78% and 84%). The Grandio Flow shows mechanical properties that are comparable to the average filled universal hybrids (between 70% and 80%).

It is hypothesized that a composite with high mechanical properties – modulus of elasticity, flexural strength, tensile strength and fracture toughness – would better resist to occlusal loads than a composite with low mechanical properties. From the above results it can thus be expected that the nanofilled composites are able to resist to these stresses at least as well as the universal composites.

One of the most surprising results in this study is that the production of flowable composites which mechanical properties are comparable to universal micro hybrid composites is now possible by adding nanoparticles, while other flowable composites had lower mechanical properties [23]. In addition, by increasing the inorganic fraction, it would logically counteract their main disadvantage, i.e. higher polymerization shrinkage than for the non-flowable but this still needs to be investigated.

4.4. Irradiation and degree of conversion

The samples used for the measurements of the mechanical properties were irradiated with a halogen curing lamp during 60 s on both sides in order to achieve the optimal degree of conversion. Unfortunately, restorations are often done under conditions that are far from the ideal and thus, as the degree of conversion can be significantly lower than for *in vitro* specimen, we can reasonably suppose that the physical and mechanical properties of the

restorations are significantly lower as well. In order to illustrate this, Figure 7 and Figure 8 compare the degrees of conversion reached with a halogen as well as with a LED curing unit used in accordance with manufacturers' instructions, respectively for the Grandio and the Supreme. Degrees of polymerization obtained with the XL-3000 are all stable within the three first millimeters of the samples. Above that value, the degree of conversion of all the materials tested decreases more or less dramatically, depending on the composite tested.

In this study we used the Freelight 2 to measure the degree of conversion obtained with a LED lamp compared with a halogen lamp. Degrees of conversion within the first millimeter of depth are quite close for the LED and the halogen, except for the Grandio Flow which showed very lower degrees of conversion with the LED. Whatever the composite, the 10 s irradiation time recommended with the Freelight 2 is clearly not sufficient. Indeed, even at a depth of 2 mm – which is traditionally the maximum thickness of composite to be cured in one layer – there is an important reduction of the degree of conversion. It is clearly insufficient at 3 mm. These results are in accordance with those of Rahiotis *et al.* [25] and of Tarle *et al.* [26]. However, Bala *et al.* [27] found no significant difference between DC of composites irradiated with halogen or LED curing units but they used both systems with an exposure time for 40 s, which eliminates an advantage of LED lamps on halogen ones according to manufacturers, i.e. they are time saving. Higher standard deviations related to irradiation with the LED curing unit show that this procedure seems here to be less reproducible than photopolymerisation using a halogen lamp.

The higher standard deviations observed with the degrees of conversion measured for the microfilled composites are probably due to the fact they contain aggregates of prepolymerized organic matrix. The Raman spectrophotometry is indeed a very local technique, i.e. the spectrum measured is taken on a microscopic surface of the sample. From a point to another, spectra were probably taken on the actual organic matrix of the composites as well as on the prepolymerized organic filler particles.

From the important decrease of the degree of conversion measured with the LED compared with the halogen it can be supposed that the mechanical properties will decrease as well. Further studies need to be conducted.

5. Acknowledgements

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5. RHEOLOGICAL PROPERTIES OF FLOWABLE RESIN COMPOSITES AND PIT AND FISSURE SEALANTS

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ABSTRACT

Objectives: The purpose of this research was to determine the viscoelastic properties of commercially available flowable resin composites and resin-based pits and fissures sealants. The weight percentage of filler particles and the morphology of the filler particles were also investigated.

Methods: Eight flowable resin composites (Admira Flow, Filtek Flow, Flow Line, Grandio Flow, Point-4 Flowable, Revolution Formula 2, Tetric Flow and X-Flow) and four pits and fissures sealants (Clinpro, Delton FS⁺, Estiseal F and Guardian Seal) were tested. Rheological measurements were performed using a dynamic oscillation rheometer. The filler weight content was determined by thermogravimetric analysis (TGA) and the morphology of the particles was investigated by scanning-electron microscopy (SEM).

Results: Flowable resin composites are non Newtonian, shear-thinning materials. As the shear rate increased, the complex viscosity decreased drastically. They all showed elasticity even at the lowest frequencies. They also all showed thixotropy. Pits and fissure sealants are non Newtonian, very low viscosity fluids. No correlation was found between the rheological properties and the filler weight content or the particles' shape.

Significance: Huge differences are observed in the viscosity and flow characteristics of flowable resin composites that can have a potential influence on their clinical behavior during handling and thus on their clinical indications. Pits and fissures sealants show very different rheological properties from one to another.

KEYWORDS

Resin composites, rheology, viscoelasticity, flowable, pits and fissures sealants, filler particles, complex viscosity, thixotropy

1. Introduction

Since resin composite restorations were developed as aesthetic and more conservative alternative to silver amalgams, many efforts have been made to improve their physical and mechanical properties by the development of new monomers, new filler particles and surface treatments as well as new photoinitiation systems and many other important topics [1, 2, 3, 4, 5, 6, 7, 8].

Resin composites are more time-consuming and by far more technique sensitive than silver amalgam restorations. Thus, the handling characteristics are of major importance for the final quality, success rate and life span of composite restorations. Indeed, the consistency and flow characteristics of the material are directly related to the ability of the resin composite to be correctly placed and shaped in the cavity without formation of gaps between the material and the cavity margins or between successive layers of the restorations. Resin composites are to adhere to tooth tissues and not to instruments [9, 10, 11, 12, 13, 14].

The first generation of flowable resin composites was introduced in late 1996. They were created mainly by retaining the same small particle size of traditional hybrid composites, but reducing the filler content and consequently the viscosity of the mixture [15]. These materials can be manipulated using a syringe and a loading tip and injected where traditional instruments' access is difficult or impossible, because of the low viscosity of these materials.

Throughout the years, various techniques were used as an attempt to characterize the rheological properties of resin composites. Ferracane *et al.* [9] used a rotational cone and plate viscometer to determine the viscosity characteristics and working-time of chemically cured composites. Opdam *et al.* [16] compared the consistency of several resin composites by a press method. I.-B. Lee *et al.* [12] characterized the viscoelastic properties of resin composites using a dynamic oscillatory rheometer and, more recently, using a vertical oscillation rheometer [14]. J.-H. Lee *et al.* studied the rheological properties of resin composites with variations in monomer and filler composition using a dynamic oscillatory rheometer [13].

The consistency and flow-characteristics of flowable resin composites as well as pits and fissures sealants are the most obvious since their handling is mainly based on a controlled flow of the material in the cavity or in the pits and fissures of teeth. However, the rheological properties of flowable resin-based materials are complex and it is known that there are large differences in the consistency of flowable resin composites from one manufacturer to another [15]. Therefore, there is a need for a classification of these materials as a function of their

clinical indications. Indeed, there is an obvious interest to use very low viscosity materials to seal the pits and fissures of the occlusal anatomy but one may prefer to use resin composites with higher consistency in order to achieve the restoration of class V cavities.

The purpose of this study was to understand the structure and the dynamic behavior of commercially available flowable resin composites and pits and fissures sealants by the way of dynamic rheological measurements as well as morphological analysis of their inorganic fraction in order to precise their clinical indications as a consequence of their flow characteristics. Rheological measurements were performed using a dynamic oscillatory rheometer. The inorganic fraction was analyzed by thermogravimetric analysis (TGA) to determine the weight percentage of filler particles and by scanning-electron microscopy (SEM) to investigate the morphology of the particles.

2. Materials and methods

2.1. Resin composites and pit and fissure sealants

Eight flowable resin composites and four pit and fissure sealants were tested in this study. They are listed in Table 1. It is to be noted that Admira Flow has a particularity in the fact that it is issued from theOrmocer (Organically Modified Ceramics) technology.

Material	Manufacturer	Shade	Batch
Resin composites			
Admira Flow	Voco (Cuxhaven, Germany)	A2	500244
Filtek Flow	3M-ESPE (St. Paul, MN, USA)	A3	4GJ
Flow Line	Heraeus-Kulzer (Wehrheim, Germany)	A2	010103
Grandio Flow	Voco (Cuxhaven, Germany)	A3	450086
Point-4 Flowable	Kerr (Orange, CA, USA)	A3	408419
Revolution Formula 2	Kerr (Orange, CA, USA)	A3	4-1336
Tetric Flow	Ivoclar-Vivadent (Schaan, Liechtenstein)	A3	G05246
X-Flow	Dentsply-De Trey (Konstanz, Germany)	A3	501000570
Pits and fissures sealants			
Clinpro	3M-ESPE (St. Paul, MN, USA)	N/A	5FG
Delton FS ⁺	Dentsply-De Trey (Konstanz, Germany)	N/A	040825
Estiseal F	Heraeus-Kulzer (Wehrheim, Germany)	N/A	010027
Guardian Seal	Kerr (Orange, CA, USA)	N/A	403412

Table 5-1: List of the materials tested.

2.2. Rheological measurements

Rheological measurements on all the materials tested in this study were performed using an Advanced Rheometric Expansion System (ARES, TA Instruments Inc., New Castle, DE, USA) at a temperature of 23°C.

2.2.1. Flowable resin composites

A parallel plates viscometer module with a diameter of 25 mm was used to measure the rheological properties of the flowable resin composites tested. The gap between the plates was 1 mm. Strain sweep tests were performed to check the range of uniform output signal so that all the following measurements were carried out in the linear range of deformation of each material. A time sweep test was then made during 7200 s at a frequency of 0.1 rad/s after materials had undergone a pre-shear at a rate of 1 s^{-1} for a complete 360° revolution of the lower plate in order to destroy the internal structure of the samples and to reveal any potential thixotropic behavior. After, a frequency sweep test was performed from 100 rad/s to 0.01 rad/s to determine the variation of the complex viscosity (η^*), storage (elastic) shear modulus (G'), loss (viscous) shear modulus (G'') and loss tangent ($\tan \delta$) as a function of the frequency.

2.2.2. Pit and fissure sealants

Due to the very low viscosity of pits and fissures sealants, a cone and plate viscometer module with a diameter of 50 mm and a cone angle of 0.02 radian was chosen. The sequence used for the rheological measurements on the pits and fissures sealants was the same as the one used for the flowable resin composites except that no time sweep tests were performed and the frequencies analyzed in the frequency sweep tests ranged from 100 rad/s to 0.1 rad/s. Indeed, due to the very low viscosity of pits and fissures sealants, no satisfactory signal was recorded between 0.1 rad/s and 0.01 rad/s.

2.3. Weight percentage of filler particles

The weight percentage of filler particles was determined using thermogravimetric analysis (TGA/SDTA861^e, Mettler-Toledo, Greinfensee, Switzerland). Weight changes were evaluated as a function of time and temperature during a thermal program ranging from 30 to 900°C at the rate of 10°C/min in normal atmosphere followed by air cooling to room temperature. The calculated ratio between the final weight of the sample and its nominal weight is assigned to the inorganic fraction. Three samples of each material were analyzed.

2.4. Morphology of the filler particles

The filler morphology was determined using scanning-electron microscopy (SEM). Unpolymerized monomers were removed by a washing technique: 0.5 g of each material was dissolved in 4 ml of acetone and centrifuged for 5 min at 700 g. This process was repeated three times using acetone and followed by three others with chloroform for a further washing and to ensure a complete elimination of the unpolymerized resin. The remaining fillers - including prepolymerized fillers - were suspended in 2.5 ml of absolute ethanol, smeared on a glass slide (7.5 x 2.5 cm) and dried at 37°C during 6 hours. After gold-coating, fillers were observed by SEM (Leica Stereoscan S-260, Cambridge, UK) at 5,000 and 10,000 magnifications.

3. Results

3.1. Rheological measurements

3.1.1. Flowable resin composites

The evolution of the complex viscosity at 0.1 rad/s of the flowable composites tested as a function of the time after destructurection is presented in Table 2.

Material	Complex viscosity (Pa.s) at 0.1 rad/s		Time constant τ
	t = 0 s	t = 7,200 s	
Admira Flow	304.73	939.18	1822.16
Filtek Flow	30286	28344	N/A
FlowLine	3692.43	14718.4	2536.14
Grandio Flow	86.977	740.16	2492.21
Point-4 Fl.	6817.75	10792	2562.59
Revolution F.2	832.75	2757	2431.67
Tetric Flow	141.53	968.06	4098.86
X-Flow	706.79	2420.4	583.77

Table 5-2: Complex viscosity (η^*) as a function of the time after destruction of the flowable resin composites tested.

Figure 1 shows the viscosity as a function of the time reported to the viscosity without any deformation (i.e. at rheological equilibrium, relative viscosity = 1) of all the materials tested. The complex viscosity at t = 0 s is much lower than the one at t = 7,200 s and increases gradually for all the materials tested except for Filtek Flow which complex viscosity shows a huge overshoot phenomenon (i.e. the viscosity is higher than the one at rest)

immediately after deformation and then returns progressively to equilibrium after around 2,000 s.

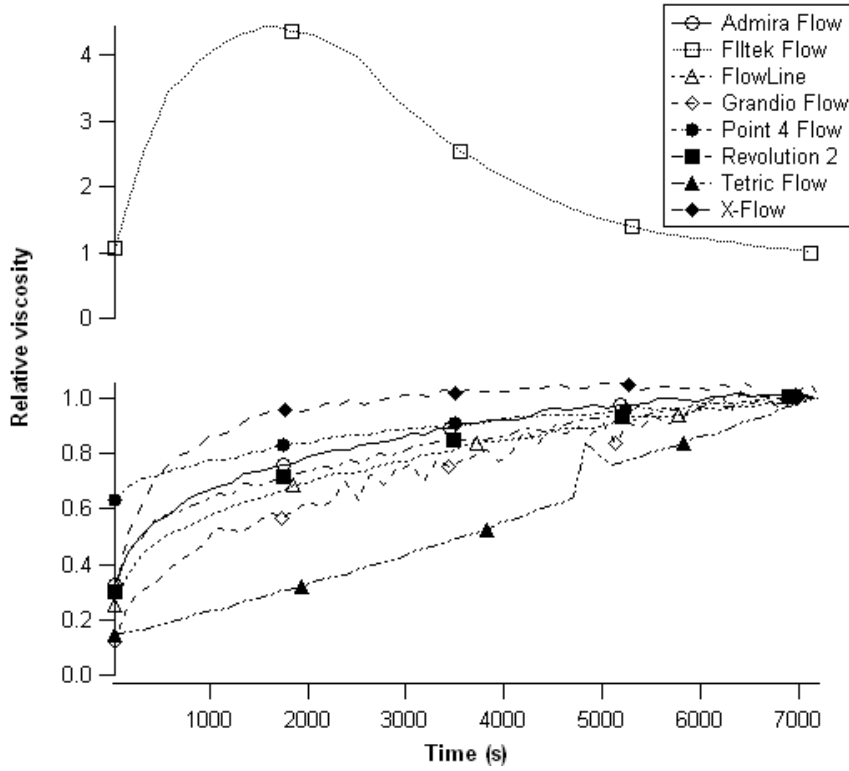


Figure 5-1: Relative viscosity of the flowable resin composites as a function of the time after deformation (the 1 value is the viscosity of the sample without any deformation).

As an attempt to characterize the evolution of the complex viscosity after destructurement of the resin composites, the results presented above were modeled in order to isolate the speed of return to equilibrium. To obtain this, the complex viscosity was expressed as follows:

$$\eta_{rel} = \frac{(\eta_{7,200s} - \eta_t)}{\eta_{7,200s}}$$

on a logarithmic scale. The curve fitting gives a straight line which equation is written as follows:

$$y = a \cdot \exp\left(\frac{-x}{\tau}\right)$$

where τ is the time constant of the material. This is presented in Figure 2. Only FlowLine, Point-4 Flowable and Revolution Formula 2 were represented to keep the figure easily understandable. It is to be noted that the three slopes are very close to each other. Table 2 presents the time constant of each resin composite as calculated using this method.

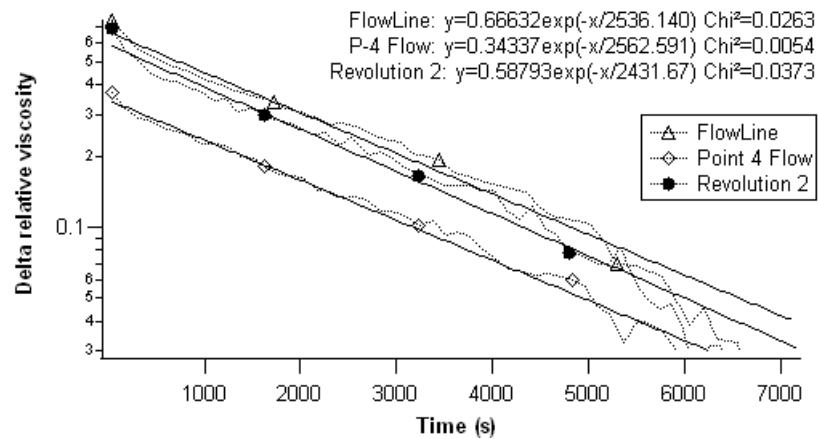


Figure 5-2: Modeling of the return to equilibrium of the flowable resin composites as a function of the time after deformation.

The complex viscosities versus frequency of the eight resin composites tested are presented in Figure 3. They all decreased as frequency increased, indicating strong non Newtonian behavior and no hint of a Newtonian plateau even at the lowest frequencies. Globally, the difference in the complex viscosity of the materials between low and high frequencies lies between two and three decades. Filtek Flow has the highest viscosity whatever the frequency. Grandio Flow shows the lowest complex viscosity at low frequencies and Admira Flow shows the lowest complex viscosity at high frequencies. However, Tetric Flow has the lowest complex viscosity at intermediate frequencies. At very high frequencies, Revolution Formula 2 has the lowest complex viscosity.

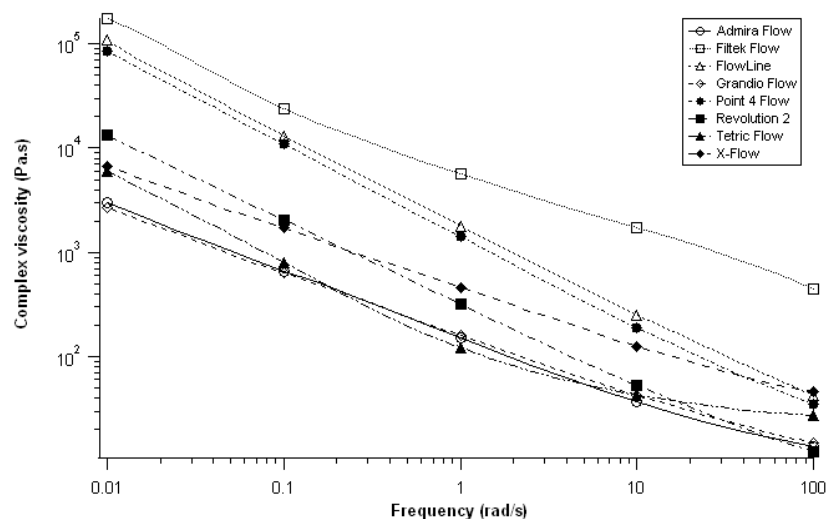


Figure 5-3: Complex viscosity (η^*) vs. frequency for the flowable resin composites tested.

Figure 4 shows the storage moduli of the flowable resin composites. The low slopes at low frequencies (except for Admira Flow, Grandio Flow and X-Flow) indicate a very strong elasticity of the materials. Confirming the viscosity results, no transition to terminal behavior (i.e. simple liquid flow) can be observed even at the lowest frequencies.

The storage shear modulus of all the flowable resin composites tested increases as the frequency increases. Filtek Flow has the highest storage shear modulus whatever the frequency. Tetric Flow has the lowest storage modulus, except at low frequency where Grandio Flow has the lowest one.

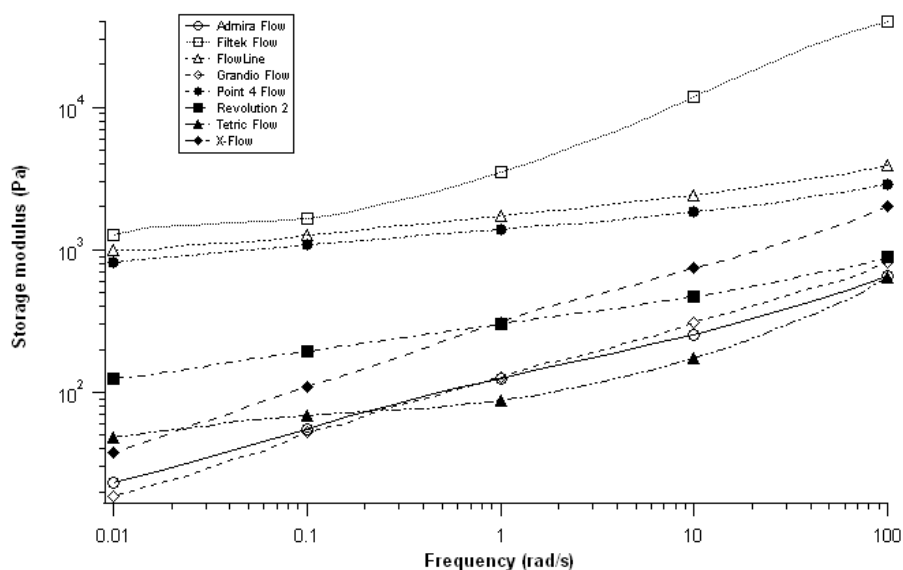


Figure 5-4: Storage modulus (G') vs. Frequency of the flowable resin composites tested.

For clarity purpose, the values of the loss modulus and the loss tangent are not presented because did not give additional information on the rheological properties of the materials tested.

3.1.2. Pit and fissure sealants

The complex viscosities versus frequency of the four pits and fissures sealants tested are shown in Figure 5. They very slightly decreased as frequency increased except for the Estiseal F which showed higher variation of complex viscosity. They were consequently non Newtonian. The difference in the complex viscosity at low and high frequencies lied around half a decade except for Estiseal F for which it lied around one decade. As for the flowable resin composites, no Newtonian plateau at the lowest frequencies can be observed.

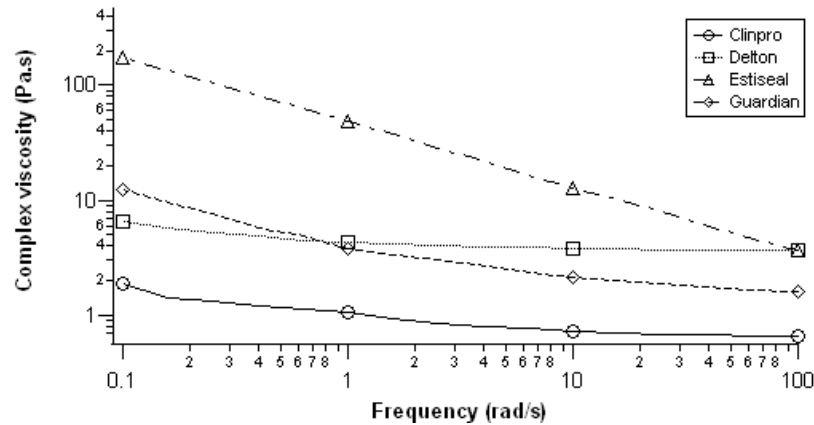


Figure 5-5: Complex viscosity (η^*) vs. frequency of the pit and fissure sealants tested.

Figure 6 present the storage moduli of the pits and fissures sealants tested. They all increased as the frequency increased. Again, no sign of a transition to terminal behavior is observed.

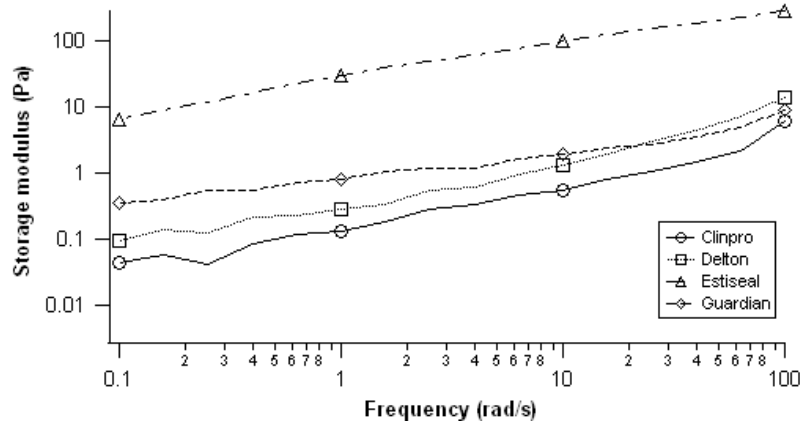


Figure 5-6: Storage modulus (G') vs. Frequency of the pit and fissure sealants tested.

3.2. Weight percentage of filler particles

The mean values and standard deviations of the weight percentage of fillers of all the materials tested are shown in Figure 7. Averages for the flowable resin composites ranged from 45.0% for the Revolution Formula 2 to 77.8 % for the Grandio Flow. For the pits and fissures sealants, averages varied from 6.5% for the Clinpro to 54.3% for the Delton FS⁺.

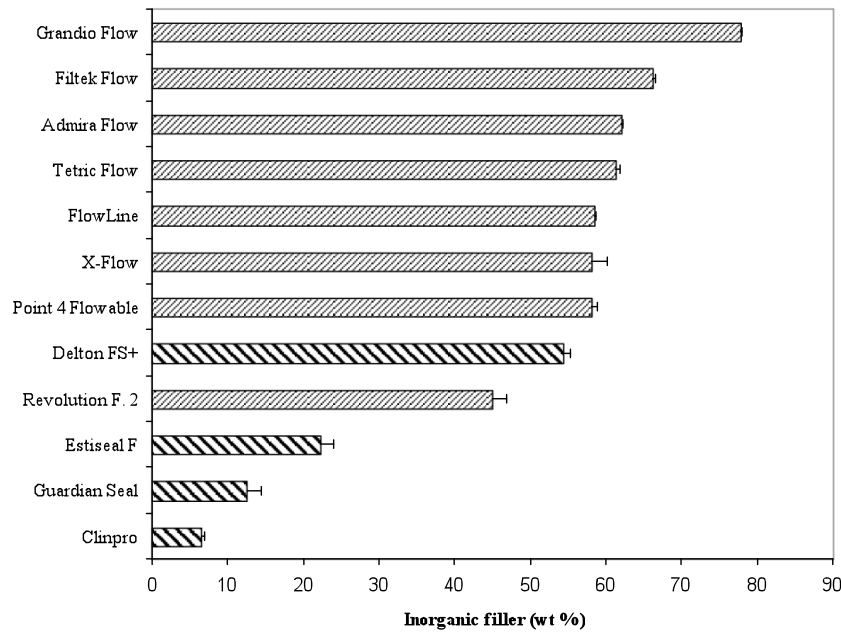


Figure 5-7: Mean values and standard deviations of the percentage of fillers by weight of all the materials tested.

3.3. Morphology of the filler particles

The SEM microphotographs of the filler particles that are included in the flowable resin composites are shown in Figure 8. Inserts are twice the magnification of the main pictures. Filtek Flow and Point-4 Flowable showed rather spherical particles. More irregular shaped particles were found in Admira Flow, Flow Line, Grandio Flow, Revolution Formula 2, Tetric Flow and X-Flow.

Figure 9 present the filler particles that can be found in the pits and fissures sealants. It is to be noted that for an unknown reason, no satisfying image of the particles of the Clinpro could be obtained. Delton FS⁺, Estiseal F and Guardian Seal showed irregular shaped particles. Delton FS⁺ showed bigger particles than the two others.

RESIN COMPOSITES

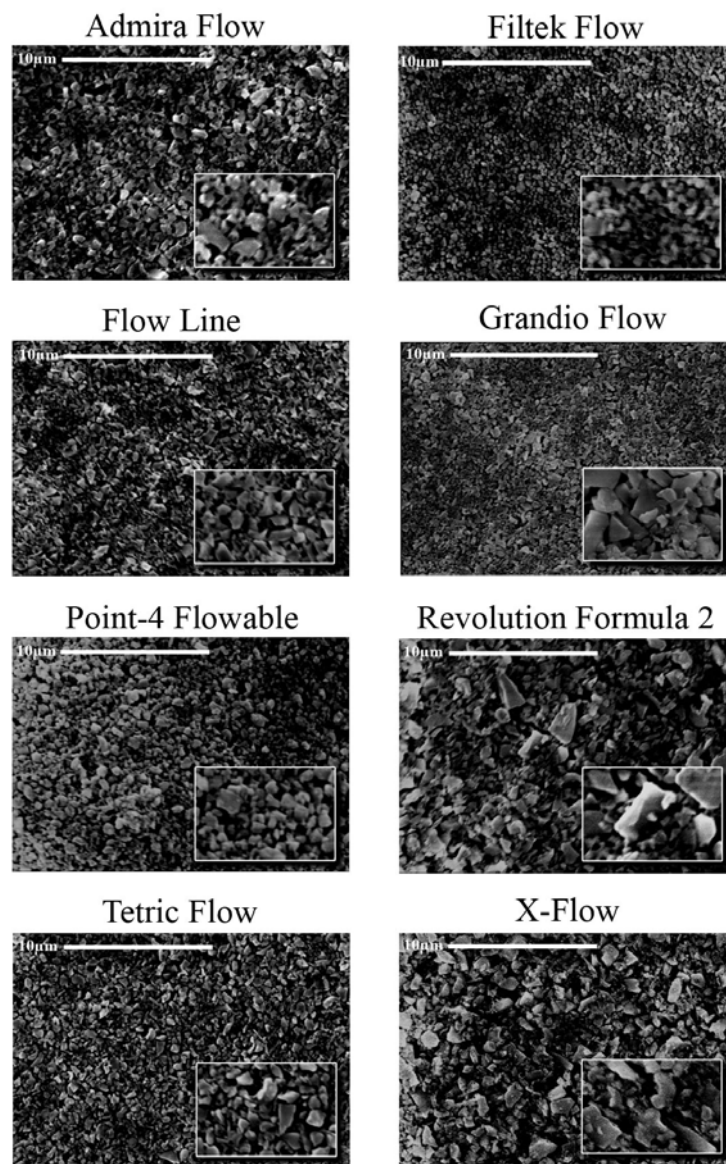


Figure 5-8: Fillers of the flowable resin composites by scanning-electron microscopy at 5000x magnification (10,000x in the inserts).

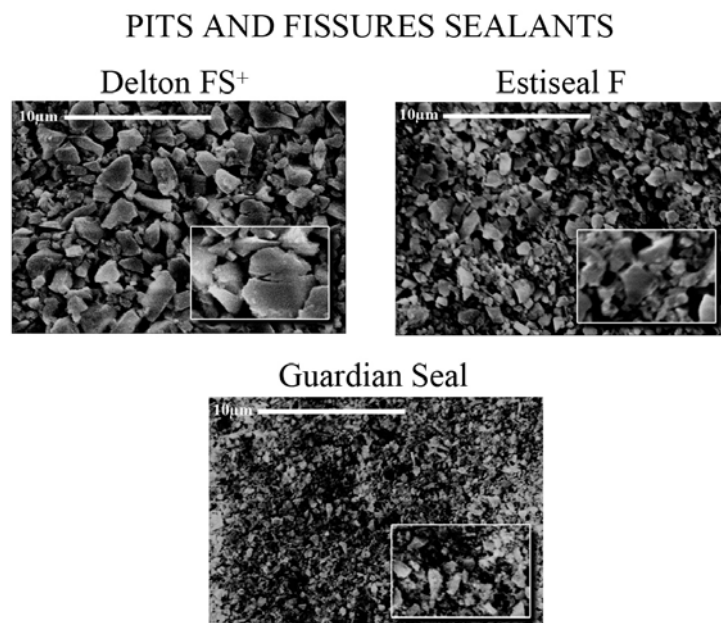


Figure 5-9: Fillers of the pit and fissure sealants by scanning-electron microscopy at 5000x magnification (10,000x in the inserts).

4. Discussion

All the flowable resin composites tested in this study are viscoelastic materials. They are all non Newtonian and show a shear-thinning behavior, i. e. their complex viscosity decreases as the frequency increases. This is in accordance with the results obtained by I.-B. Lee *et al.* [12, 14] and J.-H. Lee *et al.* [13]. The fact that there is no hint of a Newtonian plateau for the complex viscosity of the flowable composite even at the lowest frequencies on Figure 2, combined with the fact that there is no drop of the storage modulus on Figure 3 at low frequency indicates a solid-like behavior at rest.

From the results of the complex viscosity and the storage modulus versus frequency, three groups of flowable resin composites can be observed. The first one, including Filtek Flow, FlowLine and Point-4 Flowable, has higher viscosities and storage moduli than the others. In addition, the slope of their storage moduli at low frequencies is close to the horizontal, indicating a very strong elasticity and thus a strong solid-like behavior. At high frequencies, Filtek Flow shows a pretty higher viscosity than FlowLine and Point-4 Flowable. The second group (Revolution Formula 2 and Tetric Flow) shows materials that have a lower viscosity than the previous one but which storage moduli at the lowest frequencies show similar properties than for the first group, i.e. low slopes and thus strong solid-like behavior. The third group, including Admira Flow, Grandio Flow and X-Flow, has rheological properties similar to those of the second group except that their storage moduli show higher

slopes at low frequencies, indicating less solid-like behavior than for the other flowable resin composites tested.

Clinically, this means that a composite that belongs to the third groups has a better ability to flow by itself in small cavities or fissures than the others. On the contrary, those belonging to the first or the second group stay better in place when manipulated and are less subject to creep flow. But this has to be put in balance with the fact that, as demonstrated in Figure 1, their viscosity decreases dramatically when submitted to an important destructure. Indeed, flowable resin composites are most often handled using a syringe and the flow of the materials through the syringe's tip strongly affects their internal structure and thus highly reduces their viscosity. Further studies are needed to better understand their behavior during the seconds and minutes after strong destructure.

Except for Filtek Flow, the complex viscosity of all the resin composites tested returns to equilibrium while their internal structure builds up again. This follows an exponential law, as showed in Figure 2. Globally, the rate remained pretty much the same whatever the material. The overshoot observed with Filtek Flow suggests a jamming phenomenon indicating that its inorganic fraction must be very close to the maximum packing limit of filler particles (in this case small spherical particles). From a clinical point of view, since resin composites are photopolymerized immediately after being handled, they are frozen in a state that is far from equilibrium. It is thus quite simple to imagine that this could have consequences on the shrinkage stress, the post-shrinkage phenomenon or even on the physical and mechanical properties of the materials. Again, further studies are needed.

The use of thermogravimetric analysis is a good method to determine the filler particles weight content of dental resin composites, as demonstrated by Sabbagh *et al.* [17] and the values obtained with this method are highly correlated with those obtained by the more traditional ashing in air technique.

No correlation could be made between the weight percentage of filler particles and the complex viscosity of the flowable resin composites. This is in accordance with the results obtained by Lee *et al.* [12]. Grandio Flow, which has the highest filler particles weight content (77.8 %) has the lowest viscosity at low frequencies and one of the lowest at both midrange and high frequencies. This is of major interest since this material shows mechanical properties that are comparable to those of universal hybrid composites [18] while traditional flowable composites have lower properties [19]. Adding nanoparticles in resin composites could consequently allow the production of flowable materials with both higher mechanical properties and better flow characteristics than previously. The third most filled material,

Admira Flow (62.1%), shows the lowest viscosity at high frequencies. The explanation may at least partially reside in the fact that it is actually an Ormocer and that part of its inorganic content does probably not influence its flow characteristics.

All the pits and fissures sealants tested in this study are non Newtonian. They are low viscosity materials but show an elastic behavior at low frequencies. As for the flowable resin composites, no correlation could be made between the complex viscosities and the filler weight content of the filler particles. Estiseal F has a higher viscosity and higher storage modulus than all the other pits and fissures sealants even though Guardian Seal has more than twice its filler weight content (22.2 % and 54.3 % respectively). No measurement of the evolution of the complex viscosity after destructureation could be made because the values recorded were below the measurement threshold of the rheometer.

Most filler particles of the flowable resin composites are of irregular shape. Again, no strong correlation could be made between the particles' morphology and the rheological properties of the resin composites. However, spherical particles are found in Filtek Flow and Point-4 Flowable which both belong to the first group. A spherical shape is known to have many advantages such as to allow an increased filler load in composites [20] but also to enhance their fracture strength since mechanical stresses tend to concentrate on the angles and protuberances of the filler particles [21]. Irregular shaped particles were found in all the other composites tested. Admira Flow, Revolution Formula 2 and X-Flow showed bigger particles than the others. As for the flowable resin composites, no correlation could be made between the flow characteristics of the pits and fissures sealants and the morphology of their filler particles.

The viscosity of a resin composite is influenced by both the organic and the inorganic fraction. The type and amount of each monomer used are directly responsible for the viscosity of the organic matrix. This one is then strongly influenced by the amount, shape, size and surface treatment of the filler particles that are added to the composite. Since no correlation was found between the viscosity and the shape and weight content of filler particles, research must probably be undertaken to investigate the influence of various surface treatments of the particles that can influence their surface energy and consequently the physical and chemical interactions between particles and with the organic fraction.

Since the filler particles content of pits and fissures sealants is pretty low, it is possible that their viscosity is quite much influenced by the composition of the organic fraction (much more than for the flowable resin composites), which highly differs from one

material to another. Unfortunately, only very poor information is available on the exact nature and content of the organic fraction of these materials.

5. Acknowledgements

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6. RHEOLOGICAL PROPERTIES OF EXPERIMENTAL BIS- GMA/TEGDMA FLOWABLE RESIN COMPOSITES WITH VARIOUS MACROFILLER/MICROFILLER RATIO

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ABSTRACT

Objectives: The purpose of this study was to investigate the rheological behavior of resin composites and to evaluate the influence of each component, organic as well as inorganic, on their viscoelastic properties by testing model experimental formulations.

Methods: Several unfilled mixtures of Bis-GMA and TEGDMA were prepared as well as experimental flowable resin composites using a Bis-GMA/TEGDMA 50/50 wt% mixture as organic fraction filled at 60 % in weight with varying ratios of silanated Barium glass (1 μm) and partially hydrophobic fumed silica (0.1 μm). Their rheological properties were investigated using dynamic oscillatory rheometers. Transmission-electron microscopy (TEM) was also performed to investigate the spatial organization of the filler particles.

Results: Unfilled Bis-GMA/TEGDMA mixtures all showed a Newtonian behavior. The experimental flowable resin composites were non Newtonian, shear-thinning fluids. As the quantity of microfiller increased, the viscosity increased and the shear-thinning behavior increased as well. In addition, the experimental composites showed thixotropy, i.e. their viscosity is a function of time after deformation. All these properties were not specifically linked to the creation and destruction of a visible network between inorganic particles, as no difference could be seen between particles' spatial organization at the equilibrium rest state or immediately after deformation.

Significance: The complex viscoelastic properties of resin composites are due to interactions between microfiller and monomer molecules. Modifying the chemical and physical properties of the particles' surface could possibly improve their flow properties and thus their clinical handling performances.

KEYWORDS

Resin composites, viscoelasticity, rheology, filler particles, complex viscosity, thixotropy

1. Introduction

In today's restorative dentistry, resin composites restorations are by far more popular than silver amalgams. Indeed, many efforts at improving their physical, mechanical and aesthetic properties have been undertaken since the very first dental resin composites were developed [1] and recently commercialized resin composites show very good clinical performances. A lot of studies are conducted on the development of new monomers [1, 2, 3], new filler particles and surface treatments [1, 4, 5], new photoinitiation systems and many other fundamental topics.

Viscoelasticity is another important physical property of resin composites. The rheological properties of uncured materials govern the way materials flow and thus the way the dentist handles them. This plays a huge role in the final success of composite restorations by allowing the materials to adhere to the tooth tissues and the practitioner to recreate the original anatomy, and by consequence the function, of the restored teeth.

Throughout the years, various techniques were used as an attempt to characterize the rheological properties of resin composites. Ferracane et al. [6] used a rotational cone and plate viscometer to determine the viscosity characteristics and working-time of chemically cured composites. Opdam et al. [7] compared the consistency of several resin composites by a press method. Lee et al. [8] characterized the viscoelastic properties of resin composites using a dynamic oscillatory rheometer and, more recently, using a vertical oscillation rheometer [9]. Lee et al. studied the rheological properties of resin composites with variations in monomer and filler composition using a dynamic oscillatory rheometer [10]. Mesquita et al. analyzed the visco-elastic properties of resin composites after polymerization by dynamic mechanical analysis (DMA) [11].

From the physicist's point of view, resin composites are highly filled suspensions of inorganic particles in an organic matrix, which gives these materials viscoelasticity, i.e. they have both liquid-like and solid-like behaviors. Such suspensions also usually exhibit complex rheological properties such as shear-thinning (i.e. the viscosity decreases as the shear rate increases), thixotropy (i.e. the viscosity depends on the time) or yield stress (i.e. the material does not flow if the applied stress is insufficient) [12, 13]. These properties are very useful in dentistry as they help the practitioner to restore teeth. But the main drawback of resin composites, from a rheological point of view, is that these properties are poorly controlled. A better understanding of the mechanisms that rule their viscoelastic behavior would allow

optimizing them in order to produce materials with better rheological properties and thus more appropriated handling performances.

A first study has been undertaken to characterize the rheological properties of commercially available flowable resin composites and resin-based pit and fissure sealants [14]. This study has shown that the viscosities and flow characteristics can hugely differ from one flowable composite to another as well as from one pit and fissure sealant to another, although their respective clinical indications are the same. Moreover, no correlation could be made between the weight content of filler particles and the complex viscosity of the materials tested, which was in accordance with the results found by Lee et al [8]. Furthermore, no strong correlation could be made between the particles' morphology and their viscoelastic properties.

The objective of the present study was to evaluate the influence of each component, organic as well as inorganic, on the rheological behavior of resin composites by testing model experimental formulations. A composite is by definition a mixture of several components and, in the case of dental resin composites, a mixture in which inorganic fillers are mixed with an organic matrix. The organic matrix is based on cross-linking dimethacrylated monomers, especially Bis-GMA (2,2-bis-[4-(methacryloxy-2-hydroxy-propoxy)-phenyl]-propane) and TEGDMA (triethylene glycol dimethacrylate). The inorganic fillers are most of the time a blend of Barium alumino fluoroboro silicate glass and silicon dioxide. As a consequence, unfilled Bis-GMA and TEGDMA mixtures as well as experimental flowable resin composites were used. Rheological measurements were performed using dynamical rotational and oscillatory rheometers. Scanning-electron microscopy (SEM) and transition-electron microscopy (TEM) were also performed to characterize the morphology and spatial organization of the filler particles.

2. Materials and methods

2.1. Preparation of the samples

2.1.1. Unfilled Bis-GMA/TEGDMA mixtures

Resin composites organic matrixes are most of the time a mixture of two methacrylated monomers: Bis-GMA and TEGDMA. To investigate the viscoelastic properties of the organic matrix, we prepared a range of Bis-GMA/TEGDMA mixtures. Five mixtures were prepared with a content of 20, 30, 40, 50 and 60 % of TEGDMA by weight. In addition to these mixtures, pure Bis-GMA and pure TEGDMA were also characterized. To ensure a

homogenous mixing of the two monomers and the elimination of air bubbles, samples were stored for 48 hours before testing.

2.1.2. Filled experimental composites

Filled experimental composites were prepared using a Bis-GMA/TEGDMA 50/50 mixture (wt%/wt%) to investigate the effect of the inorganic fraction on the final rheological behavior of resin composites. They were filled at 60 wt% with two types of filler particles: silanized dental glass as macrofiller (with an average diameter of 1 μm) and partially hydrophobic silica as microfiller, respectively 60/0, 57/3, 55/5, 52/8 and 50/10 wt% of the total weight of the samples. These compositions were chosen to reproduce the range of viscosities of flowable resin composites.

No photoinitiation system was added in the composites to make sure that the properties studied were not influenced by the polymerization except for the sample prepared for the transmission-electron microscopy in which a photoinitiation system consisting of a camphorquinone/amine (50%/50%) was added in a proportion of 1%.

2.2. Rheological measurements

Due to huge differences in the viscosities of unfilled and filled materials, two different rheometers were used in this study. The rheological properties of the unfilled mixtures were measured with a RheoStress 300 (Thermo Electron Corporation, Karlsruhe, Germany) equipped with a transducer able to measure extremely low viscosities. The measurements on the experimental composites were performed using an Advanced Rheometric Expansion System (ARES, TA Instruments Inc., New Castle, DE, USA). The correct calibration of both instruments was checked before the measurements to ensure the validity of the results.

All the measurements were performed at a temperature of 23°C.

2.2.1. Unfilled mixtures

Shear sweep tests from 0 to 30 s^{-1} were performed using a cone and plate geometry with a diameter of 35 mm and a cone angle of 1°. This was made to determine whether the samples exhibit Newtonian behavior or not and to measure their viscosity. Three measurements were performed for each material tested.

2.2.2. Filled experimental composites

Rheological measurements on the experimental resin composites were performed using a parallel plates viscometer module with a diameter of 25 mm. The gap between the plates was 1 mm. Strain sweep tests were performed to check the range of uniform output signal so that all the following measurements were performed in the linear range of deformation of each material. Time sweep tests were then performed during 14400 s at 0.1 rad/s after materials had undergone a pre-shear at a rate of 1 s^{-1} for a complete 360° revolution of the lower plate in order to destroy the internal structure of the samples and to reveal any potential thixotropy. The time was sufficient in all cases to restore the equilibrium structure. Next, a frequency sweep test was performed from 100 rad/s to 0.01 rad/s to determine the variation of the complex viscosity (η^*), storage (elastic) shear modulus (G'), loss (viscous) shear modulus (G'') and loss tangent ($\tan \delta$) as a function of the frequency, as described in a previous publication [14]. Three measurements were performed for each material tested.

2.3. Filler dispersion by TEM

The filler dispersion in the organic matrix was determined using transmission-electron microscopy (TEM). Two specimens of the resin composite containing 55% of macrofiller and 5% of microfiller were prepared in moulds of 25x2x2 mm. The first one was directly taken from the bulk to the mold while the second one was submitted to high shear flow before being placed in the mold to ensure a complete destructuration of the material. The samples were light-cured using two conventional curing devices (XL 3000, 3M-ESPE, St Paul, MN, USA, 650 mW/cm^2) by overlapping irradiations for a total of 40 s on both sides. Slices were then made using an ultra-microtome (Ultracut S, Reichert, Depew, NY, USA) equipped with a diamond knife (Diamond Knife Ultra 35° , Diatome, Biel, Switzerland). Micrographs were obtained using TEM (LEO922, Carl Zeiss SMT AG, Oberkochen, Germany) with an acceleration tension of 200 keV at 5,000x and 40,000x magnifications.

3. Results

3.1. Rheological measurements

3.1.1. Unfilled mixtures

Table 1 shows the viscosities of the various mixtures of Bis-GMA and TEGDMA at 23°C . They ranged from 719 Pa.s for pure Bis-GMA to 0.008 Pa.s for pure TEGDMA. All the

mixtures as well as pure Bis-GMA and pure TEGDMA are Newtonian i.e. their viscosity remains constant whatever the shear rate within the experimental range.

Composition Bis-GMA/TEGDMA (wt/wt)	Viscosity (Pa.s)
100/0	719
80/20	9.20
70/30	2.29
60/40	0.550
50/50	0.201
40/60	0.087
0/100	0.008

Table 6-1: Viscosity of the Bis-GMA and TEGDMA mixtures according to their composition.

3.1.2. Experimental composites

Table 2 shows the deformation used for each material for all the rheological measurements performed as determined with strain sweep tests in order to stay in the linear range of deformation of each experimental composite. Strain values varied from 20 % for the 60/0 composite to 0.1 % for the 50/10 one.

Material	Strain (%)
60/0	20
57/3	10
55/5	2
52/8	0.1
50/10	0.1

Table 6-2: Strain used for each of the experimental composites tested for all the rheological measurements.

The evolution of the complex viscosity of the resin composites tested as a function of time after destructure is presented in Table 3 for all the materials tested.

Material	Complex viscosity (Pa.s) at 0.1 rad/s		Time constant (s) τ (Chi ²)
	t = 0 s	t = 14,400 s	
60/0	2.4289	3.8284	N/A
57/3	17.516	51.502	2463.96 (0.05)
55/5	2058.3	7052.4	2190.7 (0.01)
52/8	31241	93432	2970.34 (0.02)
50/10	83196	177970	2893.64 (0.02)

Table 6-3: Complex viscosity (η^*) of the experimental composites as a function of time after deformation.

Figure 1 shows the relative viscosity (η_{rel}) as a function of time (i.e. the measured viscosity divided by the equilibrium value obtained after a long time in the absence of deformation) of the materials tested, except for the 60/0 mixture, for which there was no noticeable variation of the viscosity through time. For all the other experimental resin composites, the complex viscosity at $t = 0$ s is much lower than the one at the end of the test and increases gradually.

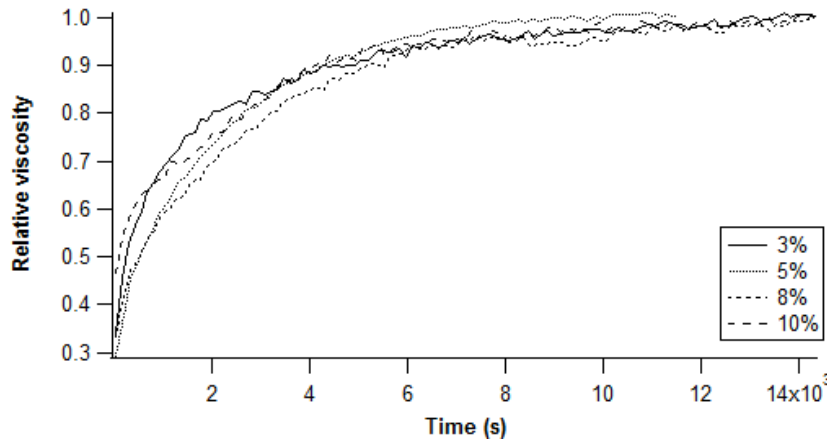


Figure 6-1: Relative viscosity of the experimental composites as a function of time after deformation (the 1 value is the viscosity of the sample without any prior deformation).

As described in a previous publication [14] and as an attempt to characterize the evolution of the complex viscosity of the resin composites after destructurection, the results presented above were analyzed in order to extract the rate of return to equilibrium. To achieve this, the complex viscosity was expressed as follows:

$$1 - \eta_{rel} = \frac{(\eta_{14,400s} - \eta_t)}{\eta_{14,400s}} \approx \exp\left(-\frac{t}{\tau}\right)$$

where τ is the time constant of the material and t the time. When plotted on a logarithmic scale, the data plotted approximately follow a straight line:

$$\ln(1 - \eta_{rel}) \approx \frac{-t}{\tau}$$

This is presented in Figure 2. Again, the 60/0 sample is not illustrated because since there was no noticeable time variation of the complex viscosity, the accuracy of such an analysis was very low. For the other experimental composites, values of the 55/5, 52/8 and 50/10 samples were shifted to avoid superposition of the results by a factor 3, 4 and 10 respectively. The slopes remain very close whatever macro-/microfillers ratio. By linear regression on $\ln(1 - \eta_{rel})$, the time constant τ can be extracted.

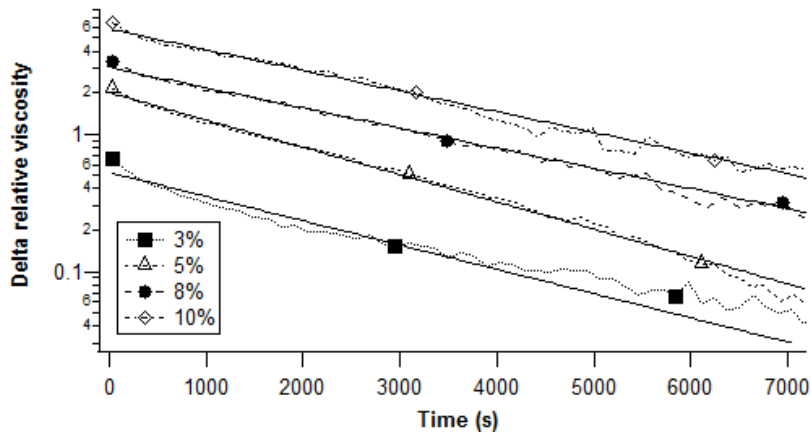


Figure 6-2: Analysis of the return to equilibrium of the experimental composites as a function of time after deformation. Values of the 55/5, 52/8 and 50/10 samples are shifter by a factor 3, 4 and 10, respectively.

Table 3 shows the time constant of each resin composite as calculated using the method described above. They ranged from 2190 s for the 55/5 composite to 2970 s for the 52/8 one and are thus very close to each other.

The complex viscosities versus frequency of the five experimental resin composites tested are shown in Figure 3. They all decreased as the frequency increased, indicating strong non Newtonian behavior and no hint of a Newtonian plateau even at the lowest frequencies. Whatever the frequency, the complex viscosity of each material increased as the microfiller content increased. In addition, the difference in the complex viscosity of the materials between low and high frequencies increased as the microfiller content increased. Globally, it ranged from less than one decade for the 60/0 composite to more than three decades for the 50/10 composite.

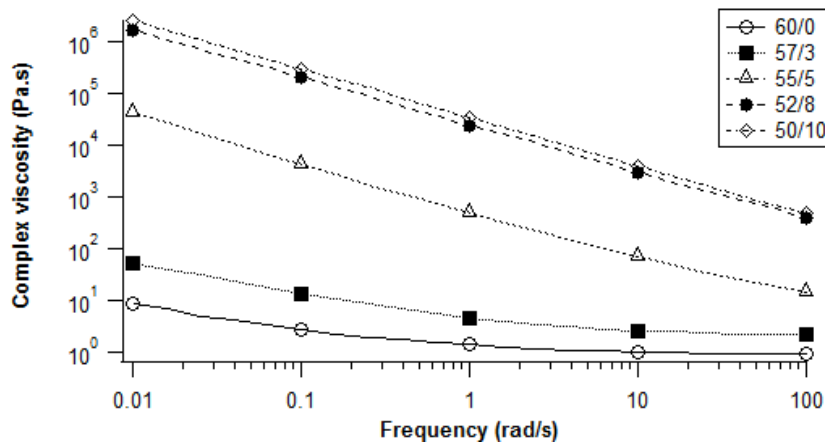


Figure 6-3: Complex viscosity (η^*) versus frequency of the experimental composites tested.

Figure 4 shows the storage moduli versus frequency of the experimental composites. As for the complex viscosities, the higher was the content in microfillers, the higher was the storage modulus whatever the frequency. In addition, the slopes of the storage moduli decreased as the microfiller content increased, indicating the onset of a very strong elasticity of the materials. As for the viscosity results, no transition to terminal behavior (i.e. simple liquid flow) can be observed even at the lowest frequencies. The same observations can be made for the results of the loss moduli versus frequency presented in Figure 5.

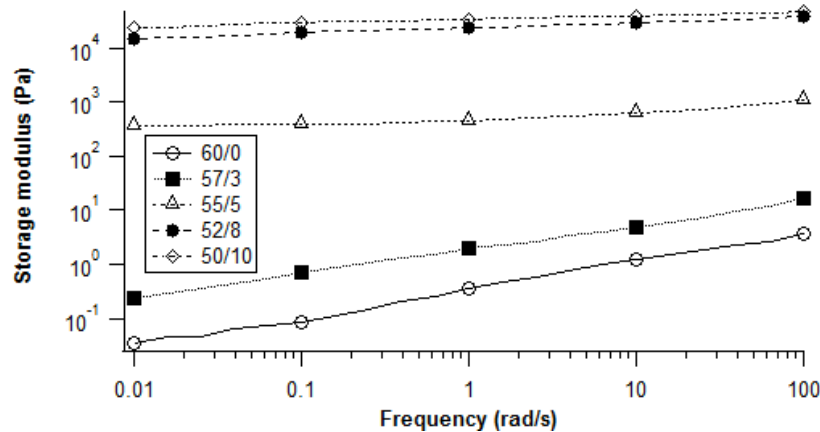


Figure 6-4: Storage modulus (G') versus frequency of the experimental composites tested.

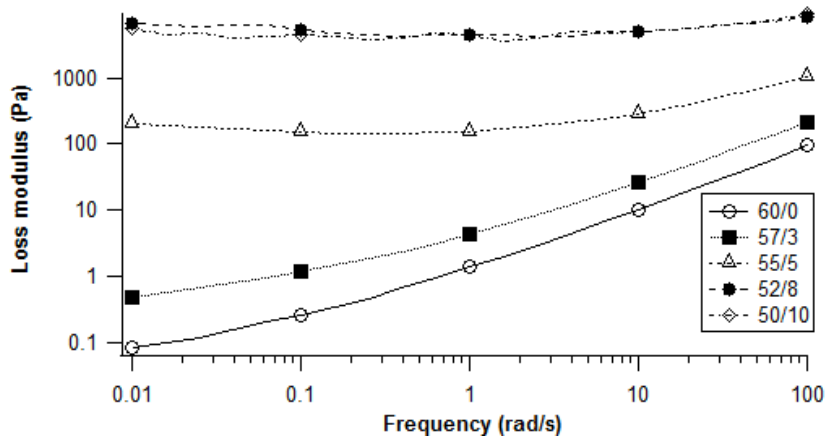


Figure 6-5: Loss modulus (G'') versus frequency of the experimental composites tested.

The loss tangents (i.e. the ratio between the loss modulus and the storage modulus) versus frequency of the materials tested are shown in Figure 6. They were less than 1 for the 55/5, 52/8 and 50/10 samples whatever the frequency, indicating a predominantly solid-like behavior of these materials. In addition, the values of the loss tangents remain globally the same at both low and high frequencies for each of the three composites which is a characteristic of gel materials [15]. The 60/0 and the 57/3 composites show a more liquid-like behavior, their loss tangent being above 1 whatever the frequency.

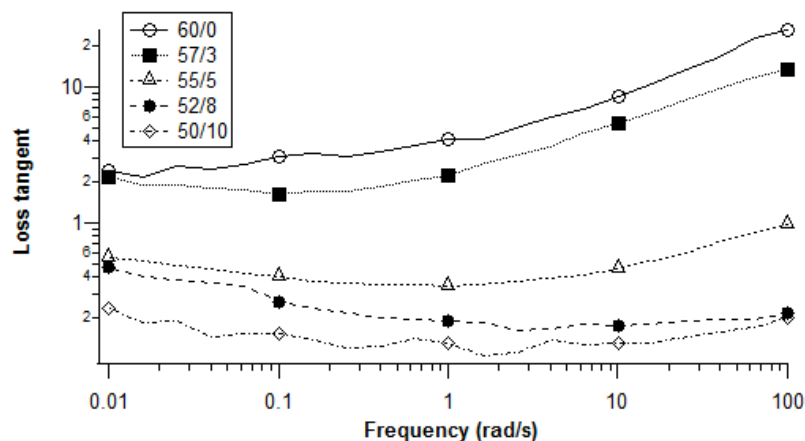


Figure 6-6: Loss tangent ($\tan \delta$) versus frequency of the experimental composites tested.

Figure 7 shows the complex viscosity of the experimental composites at 1rad/s versus the microfiller weight content. It remains almost the same up to 5 % microfiller and then increases dramatically up to 8 % and 10 % microfiller, indicating a transition to solid-like behavior.

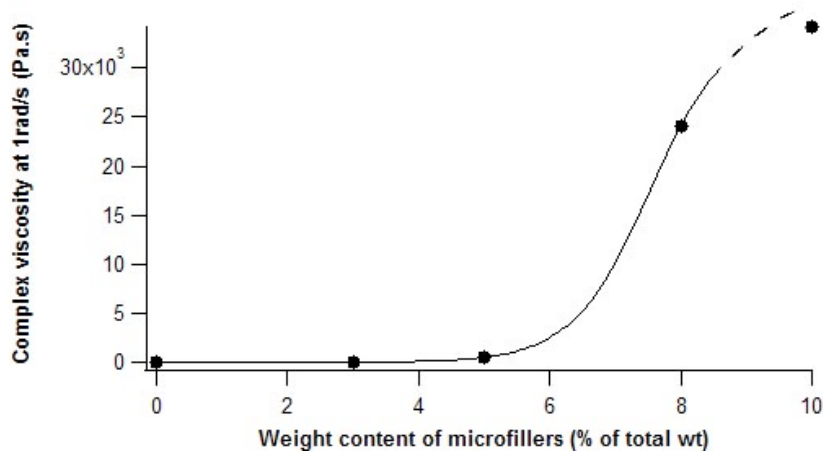


Figure 6-7: Complex viscosity at 1 rad/s versus weight content of microfillers of the experimental composites tested. The curve indicates the probable evolution of the viscosity.

3.2. Fillers dispersion by TEM

TEM microphotographs of the experimental composite with 55% macrofiller and 5% microfiller are presented in Figure 8. The upper images illustrate the material polymerized in the equilibrium structured state (i.e. after a long time without deformation before curing) while the lower images were taken for a sample polymerized immediately after severe destructuration by flow. No noticeable difference could be observed between the organization of neither the microfiller nor the macrofiller without deformation and immediately after deformation.

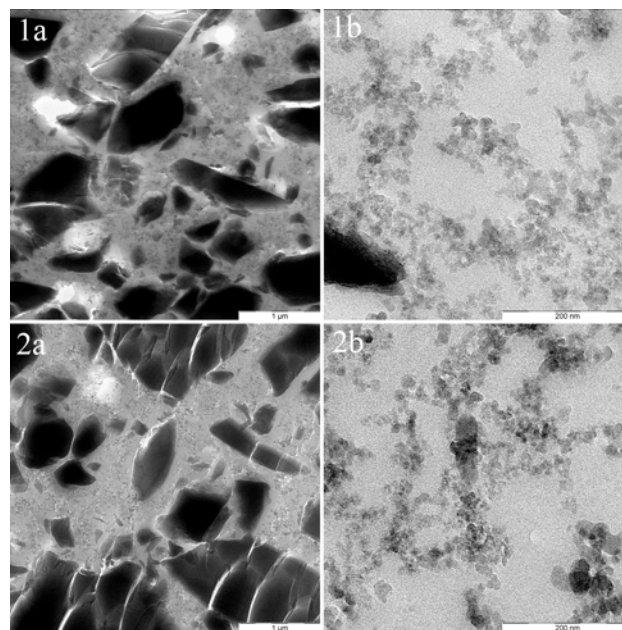


Figure 6-8: Dispersion of the fillers by transmission electron microscopy immediately after complete destructuration at 5000 x (1a) and 40,000 x (1b) magnifications and without any destructuration at 5000 x (2a) and 40,000 x (2b) magnifications.

4. Discussion

The selection of the monomers used in the organic matrix of dental resin composites has a huge influence on the reactivity, polymerization shrinkage, mechanical properties and water uptake of the final material. From the very first resin composites to the present state of the art, Bis-GMA is the main monomer used. The reasons for this are that Bis-GMA shows a relatively low polymerization shrinkage (around 6%), rapid hardening by free-radical polymerization, low volatility and good mechanical properties when cured [1, 16]. However, its main drawback is that it has a very high viscosity at room temperature and thus needs to be diluted with a low viscosity monomer in order to obtain an organic matrix that can be mixed with a satisfactory amount of inorganic fillers. But dilution with low viscosity monomers (mostly TEGMDA) leads to a major deficiency: since viscosity is correlated to the molecular weight of monomers [1] and since low molecular weight monomers have higher polymerization shrinkage [1, 16, 17], the more Bis-GMA is diluted, the more the composite will shrink when cured. As a consequence, it is generally admitted that formulating an organic matrix with a viscosity ranging from 1 Pa.s to 2 Pa.s is a good compromise in terms of workability and mechanical properties.

The viscosity measurements on the unfilled mixtures show that viscosity decreases dramatically as the content in TEGDMA increases and that both the monomers and the mixtures behave a Newtonian way, which is in accordance with the results found by J.-H. Lee et al. [10].

The addition of inorganic fillers totally changes the way the uncured materials flow. Indeed, all the experimental resin composites show a strong non Newtonian shear-thinning behavior, i.e. the complex viscosity decreases as the frequency increases. Its particular behavior is also called pseudoplasticity. This confirms the results found on commercially available flowable resin composites in a previous publication [14] as well as the results found by I.-B. Lee et al. [8] and J.-H. Lee et al. [10].

Although all the experimental resin composites tested in this study have the same total inorganic filler weight content, their rheological behavior is very different from one to another. Indeed, 60 wt% of macrofillers alone do not have a major influence on the viscoelastic properties of the material, except that they increase the Newtonian viscosity of the material and that a slight shear-thinning behavior appears. However, the more the microfillers content increases, the more the complex viscosity increases, ranging from 1.4 Pa.s with no microfiller at all to 34,000 Pa.s with 10 % microfiller at 1 rad/s. As a

comparison, adding 60 % of macrofiller to a 50/50 Bis-GMA/TEGDMA mixture changes the viscosity from 0.2 Pa.s to 1.4 Pa.s at 1 rad/s. In addition, the more the microfiller content increases, the more shear-thinning the material becomes. The complex viscosity between low and high frequencies ranges from less than one decade for the 60/0 sample to close to four decades for the 50/10 material. From these observations it can be concluded that the microfiller is the major determinant of the final viscoelastic properties of resin composites. This is in accordance with the results found by J.-H. Lee et al. [10].

Furthermore, as the microfiller content increases, the elastic moduli increases while their slopes decrease, with no hint of a drop at the lowest frequencies. The slopes of G' for the 55/5, 52/8 and 50/10 samples can even be approximated to a horizontal, which demonstrates a very strong elasticity and is a characteristic of solid materials. These elements, combined with the fact that there is no Newtonian plateau for the complex viscosities at low frequency, indicate a solid-like behavior at rest, i.e. they are yield stress materials. This solid-like behavior, which can also be found in many commercially available flowable composites [14], is also mainly influenced by the microfiller content as it becomes stronger as its content increase. These observations are confirmed by the fact that the strain limit of the linear viscosity range of the experimental composites tested decreases dramatically as the microfiller content increases, down to 0.1 % for the 52/8 and the 50/10 samples, indicating that these materials show a strong internal structure compared to the 60/0 and the 57/3 samples for which the strain limit is 20 % and 10 % respectively.

From the present observations it can be assumed that there is probably a specific point in the formulation of resin composites where rheological properties drastically change from mainly liquid-like to solid-like materials. This point can be explained as the minimal content of microfillers needed to create a gel structure. From the tangent delta values illustrated on figure 6, it can be concluded that this point lies around the 55/5 formulation, since the 60/0 and the 57/3 materials are clearly liquid-like and the 52/8 and 50/10 (as well as the 55/5) show the characteristic of a gel material. This is further confirmed on figure 7 where it is shown that the 55/5 composite stands at the beginning of the huge increase of the complex viscosity at 1 rad/s.

When they are deformed, the complex viscosity of the experimental resin composites tested in this study all decrease dramatically to a value that lies around 0.3 to 0.6 times the complex viscosity at equilibrium. Thereafter, the composites need approximately 3600 s to reach 80 % of their initial viscosity and from 7200 s to 14400 s to return to their state of equilibrium. This is called thixotropy. It means that in clinical situations, resin

composites are photo-polymerized in a state which is very far from their rheological state of rest. This could have consequences on the final mechanical properties of the materials if the decrease of the viscosity during deformation is due to some physical alteration in the material itself. It could further mean that resin composites should ideally be polymerized after re-structuration. From that point of view, and considering the present results, it further means that the time needed for the composite to reach equilibrium after deformation is much, much too long. It can hardly be conceivable that the practitioner should wait two hours before polymerizing each layer of composite.

The first hypothesis made in order to explain the thixotropic behavior of the experimental composites (i.e. huge decrease and slow recovery of the complex viscosity after severe deformation), as shown in figure 1, was that the internal structure, from a rheological point of view, is linked to the spatial organization of the microfiller. Indeed, as their complex rheological properties are linked to the quantity of microparticles and as these particles are only partially silanated, the first idea was that the decrease of the viscosity was the consequence of the destruction of a tridimensional network of microparticles linked together via hydrogen bonds and that its slow recovery was the sign of the reconstruction of the hydrogen bonds and thus the tri-dimensional network. This would be in accordance with the fact that the 60/0 composites, which contains macrofiller only, do not show any thixotropy. As an attempt to verify this, TEM was performed on the 55/5 composite polymerized with and without prior destructuration. As shown in Figure 8, no difference could be seen in the organization of both the microparticles and the macroparticles between destructured and non-destructured material, which means that the thixotropic behavior of resin composites is not mainly linked to the creation and destruction of a visible network between inorganic particles. The alternative theory is that due to of the large contact area generated by the microfiller, a very important part of the monomers interacts with the fillers surface. Interaction probably results in a layer immediately surrounding the particles where monomer mobility is more or less restricted, resulting in a significant local increase of the viscosity. Numerous studies have indeed demonstrated the existence of such a layer in dispersions of silica in rubbers where the thickness of the layer was linked to both the specific surface area of the particles and the nature and quantity of surface treatment [18, 19].

While the complex viscosity and the elastic moduli of the experimental composites are strongly influenced by the quantity of microfiller, the time needed for the complex viscosity to reach its rest value after severe destructuration of the material does not seem to be influenced by the quantity of microparticles since the slopes of all the samples on figure 2 are

approximately equivalent. Only the presence or absence of microfiller seems to play a role, as the 60/0 composite shows no thixotropy.

Further studies are needed to investigate the exact nature of the interactions that exist between both the filler particles and between particles and the organic fraction of resin composites. Further studies are also needed to determine whether mechanical properties of resin composites are linked to their rheological state and/or internal chemical or physical structure. This is required to understand what happens when the gel structure is reached, to determine whether a layer of monomers with restricted mobility exists around the particles and to understand why thixotropy does not seem to be influenced by the quantity of microparticles. These are prerequisites to future attempts to modify the rheological properties of resin composites in order to create materials with more appropriate flow properties from a clinical point of view.

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7. PHYSICAL, MECHANICAL AND RHEOLOGICAL CHARACTERIZATION OF RESIN- BASED PIT AND FISSURE SEALANTS COMPARED TO FLOWABLE RESIN COMPOSITES

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SUMMARY

Background: Numerous materials claim pit and fissure sealing as an indication. Specifically designed resin-based pit and fissure sealants but also flowable resin composites are commonly used nowadays.

Aim: The purpose of this study was to compare the mechanical and rheological properties of resin-based pit and fissure sealants to flowable resin composites.

Design: Eight flowable resin composites (Admira Flow, Filtek Supreme XT Flow, FlowLine, Grandio Flow, Point-4 Flowable, Premise Flowable, Revolution Formula 2, X-Flow) and four resin-based pit and fissure sealants (Clinpro, Delton FS⁺, Estiseal F, Guardian Seal) were used in this study. Their filler weight content was measured by thermogravimetric analysis. Mechanical properties were measured: dynamic and static moduli of elasticity, flexural strength and Vickers microhardness. Rheological measurements were performed using a dynamic oscillation rheometer.

Results: Flowable resin composites have by far better mechanical properties than pit and fissure sealants, except for Delton FS⁺. All the materials tested are non-Newtonian, shear thinning fluids. They all showed elasticity even at the lowest frequencies but elasticity differs pretty much from one material to another.

Conclusions: Resin-based pit and fissure sealants seem appropriate for preventive pit and fissure sealing. For enlarged fissures, it can be assumed that flowable resin composites with low elasticity at low frequency are more appropriate.

KEYWORDS

Pit and fissure sealants, resin composites, flowable, viscoelasticity, mechanical properties, filler particles

1. Introduction

Although occlusal surfaces represent only 12.5% of the total surfaces of the permanent dentition, they account for almost 50% of the caries in school children [1]. Tooth surfaces with pits and fissures are thus extremely vulnerable to the development of caries [2]. Pit and fissure sealants were introduced in the 1960s as an attempt to prevent occlusal dental caries. From then, their effectiveness has been demonstrated many times [3, 4].

Three main types of materials are available as pit and fissure sealants: glass ionomer cements, compomers and resins. Since the retention rate of glass ionomer cements, as well as resin modified glass ionomer cements, used as pit and fissure sealants is quite poor [5, 6], the fact that they release active F in the surrounding enamel is very important. Indeed, they exert a cariostatic effect even after they have disappeared macroscopically and this effect can reasonably be associated to increased levels of F on the enamel surface as well as to remnants of the material in the depths of the fissures [7]. For these reasons, glass ionomer cements should be considered more a F vehicle than a traditional fissure sealant [13].

Compomers were developed to match the advantages of both glass ionomer cements and resins. Only little scientific literature is available concerning the use of compomers as pit and fissure sealants. It is known that the incorporation of fluoride into resin and its release may compromise the integrity of the material [8] and that the amount of F released from compomers is considerably less than for glass ionomers [9]. However, Glavina *et al.* showed comparability with resin-based fissure sealants after a three year clinical study [10].

The caries preventive action of resin-based materials rely on the establishment of an effective mechanical obstacle to the leakage of nutrients to cariogenic microorganisms in the deeper parts of fissures [11, 12, 13]. The major criterion of success of these materials is thus based on their retention rate unlike glass ionomer sealants. They may be either filled or unfilled, and chemically or light-cured. Many studies have demonstrated the effectiveness of chemically-cured resin-based sealants in terms of retention rate [11, 14, 15]. The performance levels of light-cured resin-based sealants are similar to those of chemically-cured ones within an observation period of up to 5 years [16]. However, for longer observation periods, chemically-cured sealants seem to give better results [17] even if for obvious practical reasons light-cured materials are by far more popular among practitioners nowadays than chemically-cured ones. The addition of filler particles to resin-based pit and fissure sealants seem to have minor effect on clinical results and both filled and unfilled materials have similar retention rates [18, 19].

The use of flowable resin composites as pit and fissure sealants has also been suggested, as their formulations are quite close to those of traditional resin-based sealants and their physical and mechanical properties are supposed to be better. Their performances have been demonstrated to be comparable to those of resin-based sealants in both *in vivo* and *in vitro* studies where retention rate [12] as well as microleakage [20] and microtensile bond strength [6] were evaluated.

The purpose of this study was to compare the mechanical and rheological properties of traditional resin-based pit and fissure sealants and flowable resin composites in order to determine their ability to resist to occlusal stresses and to efficiently seal dental pits and fissures. Their inorganic fraction was also characterized. Dynamic and static moduli of elasticity, flexural strength and Vickers microhardness were measured. The inorganic fraction was analyzed using scanning-electron microscopy (SEM) and thermogravimetric analysis (TGA). Rheological measurements were performed using a dynamic oscillatory rheometer.

2. Material and methods

2.1. Materials tested

Eight commercially available flowable resin composites and four commercially available resin-based pit and fissure sealants were tested in this study. They are listed in Table 1.

Material	Manufacturer	Shade	Batch
Flowable composites			
Admira Flow	Voco (Cuxhaven, Germany)	A2	500244
Filtek Supreme XT Flow	3M-ESPE (St. Paul, MN, USA)	A3	680934
FlowLine	Heraeus-Kulzer (Wehrheim, Germany)	A2	10103
Grandio Flow	Voco (Cuxhaven, Germany)	A3	570666
Point-4 Flowable	Kerr (Orange, CA, USA)	A3	408419
Premise Flowable	Kerr (Orange, CA, USA)	A3	06-124102
Revolution Formula 2	Kerr (Orange, CA, USA)	A3	4-1336
X-Flow	Dentsply-De Trey (Konstanz, Germany)	A3	502000636
Pit and fissure sealants			
Clinpro	3M-ESPE (St. Paul, MN, USA)	N/A	5FG
Delton FS ⁺	Dentsply-De Trey (Konstanz, Germany)	N/A	40825
Estiseal F	Heraeus-Kulzer (Wehrheim, Germany)	N/A	10027
Guardian Seal	Kerr (Orange, CA, USA)	N/A	403412

Table 7-1: List of the materials tested.

2.2. Percentage and morphology of the inorganic fraction

2.2.1. Weight percentage of fillers

The weight percentage of fillers was determined using Thermogravimetric Analysis (TGA/SDTA861^e, Mettler-Toledo, Greinfensee, Switzerland). It evaluated weight changes as a function of time and temperature during a thermal program ranging from 30°C to 900°C at the rate of 10°C/min in normal atmosphere followed by air cooling to room temperature. The calculated ratio between the final weight of the sample and its nominal weight is assigned to the inorganic fraction. Three samples of each material were analyzed.

2.2.2. Fillers morphology

The fillers morphology was determined using SEM. Unpolymerized monomers were removed by a washing technique: 0.5 g of each material was dissolved in 4 ml of acetone and centrifuged for 5 min at 700 x g. This process was repeated three times using acetone and three others with chloroform for a further washing and to ensure a complete elimination of the unpolymerized resin. The remaining fillers - including prepolymerized fillers - were suspended in 2.5 ml of absolute ethanol, smeared on a glass slide (7.5 x 2.5 cm) and dried at 37°C during 6 hours. After gold-coating, fillers were observed by SEM (Leica Stereoscan S-260, Cambridge, UK) at 5,000 and 10,000 magnifications.

2.3. Mechanical properties

Five specimens of each material were prepared in moulds of 25 x 2 x 2 mm as specified in the ISO specification 4049. Samples were light-cured using two conventional curing devices (XL 3000, 3M-ESPE, St Paul, MN, USA, 650 mw/cm²) by overlapping irradiations for a total of 60 s on both sides. The same specimen was used to measure the following properties: dynamic modulus, static modulus and flexural strength, Vickers microhardness. Specimens were stored for 7 days in water at 37°C before measurement.

2.3.1. Dynamic modulus

The dynamic modulus of elasticity was measured non-destructively by the impulse excitation technique (Braem *et al.*, 1986) [21]. Each sample was set in flexural vibration by a light mechanical impulse. The signal produced was captured via a microphone placed underneath the sample by a special signal analyzer, the Grindosonic (Lemmens Electronics, Haasrode, Belgium). Modulus of elasticity (GPa) was calculated from the fundamental frequency, the mass, the width, the length and the thickness of the bar as follows:

$$E_d = 0.9465 \frac{mf_t^2}{b} \frac{L^3}{t^3} T_1$$

where m is the mass of the bar, b the width of the bar, L the length of the bar, t the thickness of the bar, f_t the fundamental frequency of the bar in flexion – which appears on the screen of the machine –, and T_1 a correction factor for fundamental flexural mode to account for finite thickness of the bar, Poisson's ratio and other constants. Poisson's ratio is the ratio of transverse strain (contraction) to axial strain (elongation) in a uniaxial tensile test [22]. When applied to dental resin composites, its value lies around 0.30 [23], which value has been taken as the mean value for all the materials tested in this study.

2.3.2. Static modulus and flexural strength

The static modulus was measured using a three-point bending setup according to the ISO-4049 specification [24]. Samples were loaded in an Instron machine (Instron 5566, High Wycombe, UK) at a speed rate of 0.75 mm/min until fracture occurred. The load and the corresponding deflection were recorded and used to calculate the modulus (GPa) and the strength (MPa):

$$E_s = \frac{Fl^3}{4bh^3d}$$

where F is the load, l the distance between the supports, b the width of the bar, h the thickness of the bar and d the deflection corresponding to the load F .

The flexural strength was calculated as follows:

$$\delta = \frac{3Fl}{2bh^2}$$

where F is the maximum load at the point of fracture, l the distance between the supports, b the width of the sample and h its height.

2.3.3. Vickers microhardness

Microhardness measurements were carried out on the fractured samples issued from the previous test with a Durimet microhardness tester (Leitz, Wetzlar, Germany). A load of 200 g was applied during 30 s on their surface. The length of the diagonal of each indentation was measured directly using a graduated eye-lens. The Vickers Hardness Number is obtained using the following equation:

$$H = \frac{1854.4 \times P}{d^2}$$

where H is Vickers hardness in kg/mm^2 , P the load in grams and d the length of the diagonals in μm [25].

2.4. Rheological properties

Rheological measurements on all the materials tested in this study were performed using an Advanced Rheometric Expansion System (ARES, TA Instruments Inc., New Castle, DE, USA) at a temperature of 23°C .

2.4.1. Flowable resin composites

A parallel plates viscometer module with a diameter of 25 mm was used to measure the rheological properties of the flowable resin composites tested. The gap between the plates was 1 mm. Strain sweep tests were performed to check the range of uniform output signal so that all the following measurements were carried out in the linear range of deformation of each material. Since flowable resin composites show thixotropy [26], a time sweep test was performed during 7200 s at a frequency of 0.1 rad/s after materials had undergone a pre-shear at a rate of 1 s^{-1} for a complete 360° revolution of the lower plate. The time sweep test was made in order to monitor the restructuration of the materials and to ensure that the following measurements were made on fully structured materials so that the results can be compared from one composite to another. After, a frequency sweep test was performed from 100 rad/s to 0.01 rad/s to determine the variation of the complex viscosity (η^*), storage (elastic) shear modulus (G'), loss (viscous) shear modulus (G'') and loss tangent ($\tan \delta$) as a function of the frequency.

2.4.2. Pit and fissure sealants

Because of the very low viscosity of pit and fissure sealants, a cone and plate viscometer module with a diameter of 50 mm and a cone angle of 0.02 radian was chosen. The sequence used for the rheological measurements on the pit and fissure sealants was the same as the one used for the flowable resin composites except that no time sweep tests were performed and the frequencies analyzed in the frequency sweep tests ranged from 100 rad/s to 0.1 rad/s. Indeed, due to the very low viscosity of pit and fissure sealants, no satisfactory signal was recorded between 0.1 rad/s and 0.01 rad/s [27].

2.5. Statistical analysis

Statistical analysis for the weight percentage of filler and all the mechanical properties was made using a one-way ANOVA and Scheffe's multiple comparison tests at $p < 0.05$ level. This was performed separately for each of the different mechanical properties.

3. Results

3.1. Percentage and morphology of the inorganic fraction

3.1.1. Weight percentage of fillers

The mean values and standard deviations of the weight percentage of fillers of the materials tested are presented in Figure 1. For the flowable resin composites, they ranged from 45.0 % for the Revolution Formula 2 to 77.8 % for the Grandio Flow. For the pit and fissure sealants, averages varied from 6.5 % for the Clinpro to 54.3 % for the Delton FS⁺.

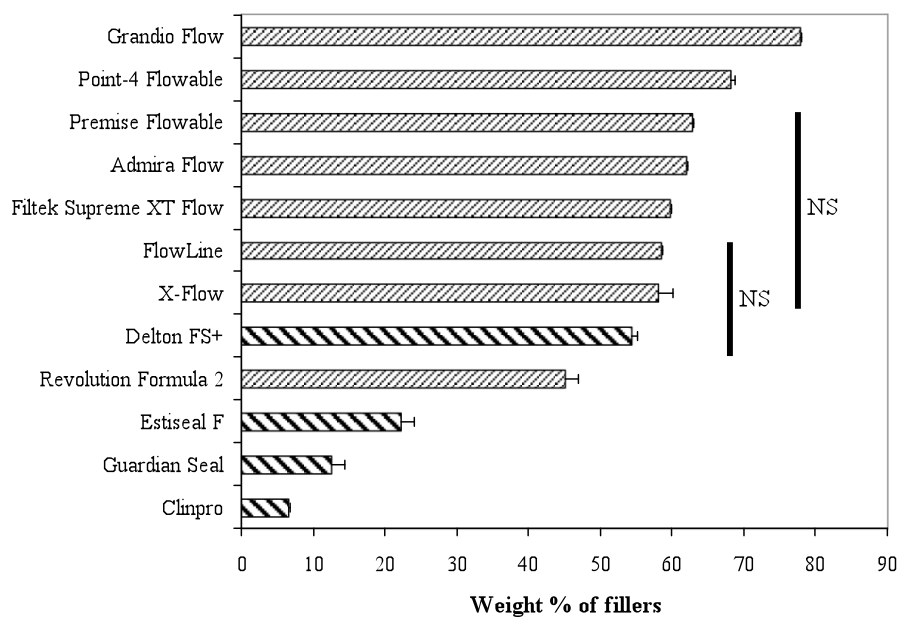


Figure 7-1: Mean values and standard deviations of the percentage of fillers by weight of all the materials tested. Vertical bars connect values that are not statistically significant ($p < 0.05$).

3.1.2. Fillers morphology

The pictures obtained by SEM of the fillers included in all the materials tested in this study are shown in Figure 2.

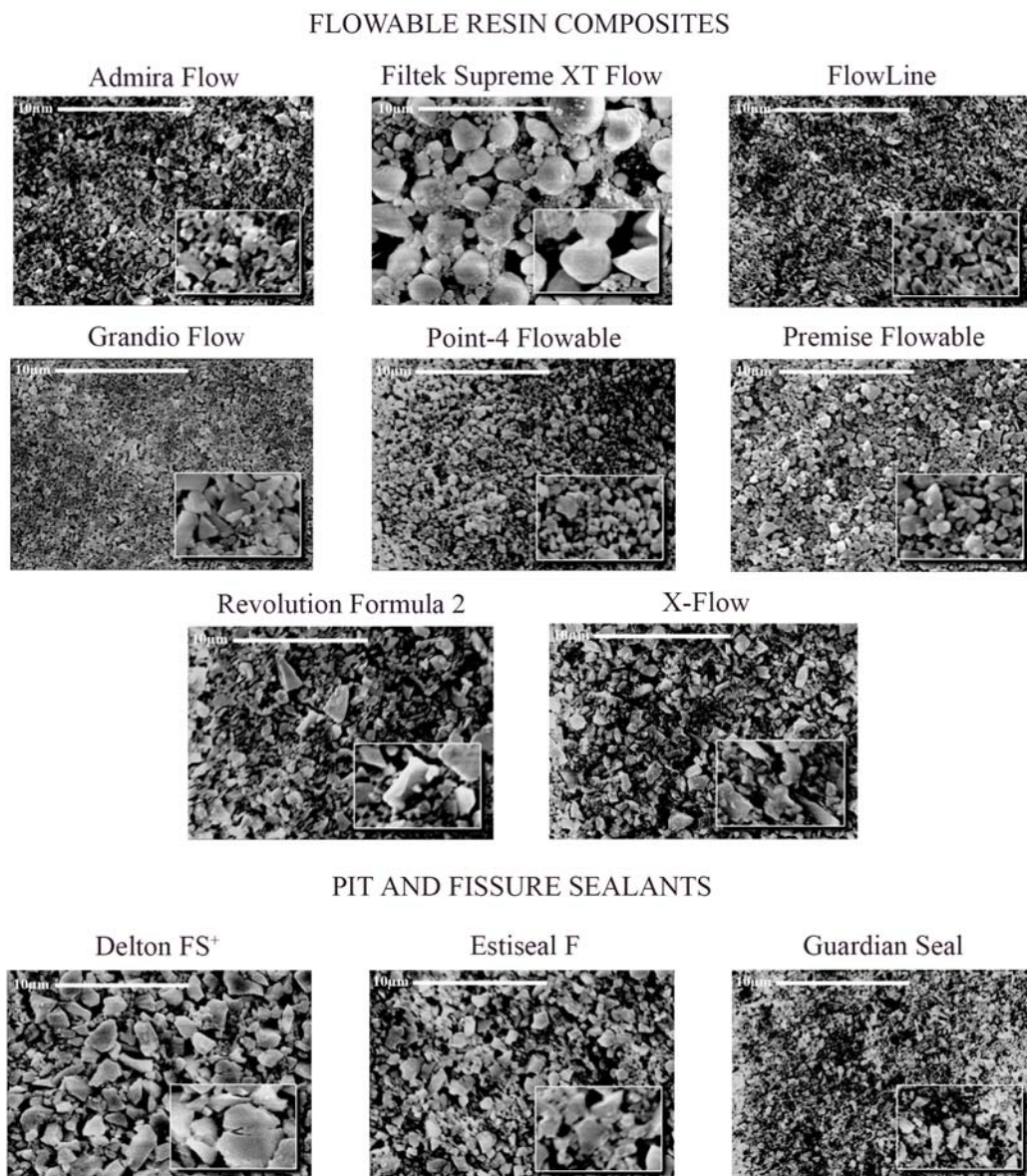


Figure 7-2: Fillers by scanning-electron microscopy at 5000 x magnification (10,000 x in the inserts) (partly from Beun et al., 2008 [27]).

For the flowable resin composites, irregularly shaped particles were found in Admira Flow, FlowLine, Grandio Flow, Revolution Formula 2 and X-Flow. Particles found in Filtek Supreme XT Flow, Point-4 Flowable and Premise Flowable were more regular, more or less spherically shaped. Filtek Supreme XT Flow contained larger particles than every other flowable composite tested.

The three pit and fissure sealants tested showed irregularly shaped particles. The particles contained in the Delton FS⁺ were larger than those included in the Estiseal F and the Guardian Seal.

3.2. Mechanical properties

The mean values and standard deviations of the dynamic moduli of elasticity of the materials tested are presented in Figure 3. For the flowable resin composites, values ranged from 3.5 GPa for the Revolution Formula 2 to 16.0 GPa for the Grandio Flow. For the pit and fissure sealants, they varied from 1.7 GPa for the Clinpro to 7.2 GPa for the Delton FS⁺.

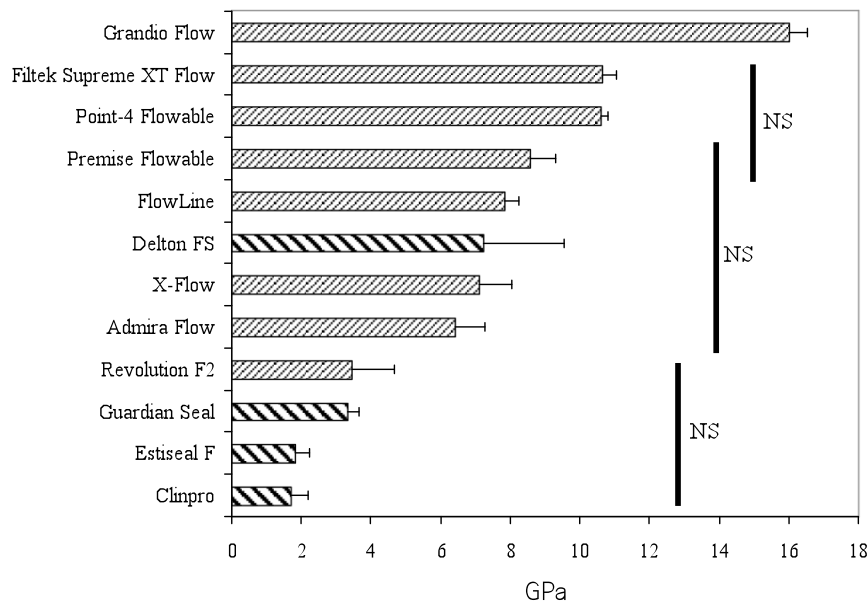


Figure 7-3: Dynamic moduli of elasticity of the materials tested. Materials that are not statistically significant ($p < 0.05$) are connected by vertical bars.

Values for the static moduli of elasticity are shown in Figure 4. Regarding the flowable composites, they varied from 1.9 GPa for the Revolution Formula 2 to 8.5 GPa for the Grandio Flow. For the pit and fissure sealants, they ranged from 1.3 GPa for the Clinpro to 3.6 GPa for the Delton FS⁺.

For the flexural strength, results are presented in Figure 5. For the flowable composites, values varied from 63.0 MPa for the Revolution Formula 2 to 116.1 MPa for the Filtek Supreme XT Flow. For the pit and fissure sealants they ranged from 39.4 MPa for the Guardian Seal to 82.6 MPa for the Delton FS⁺.

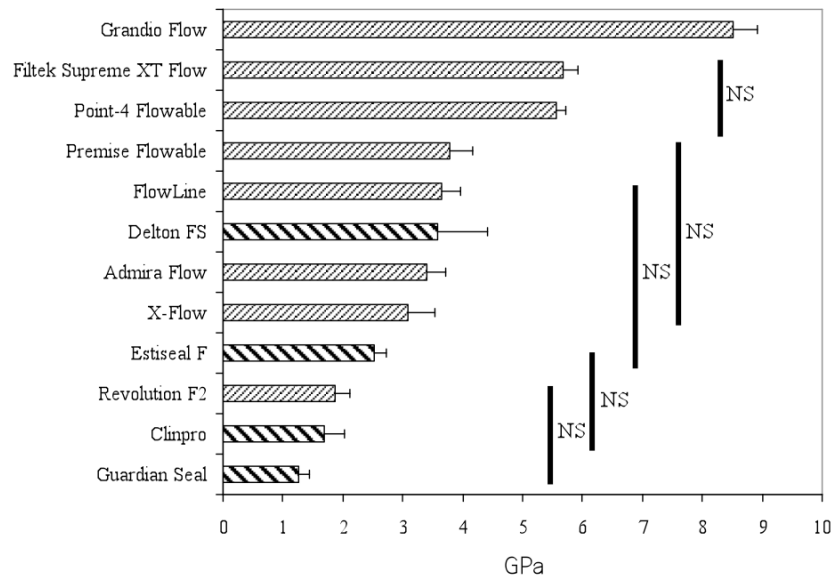


Figure 7-4: Static moduli of elasticity of the materials tested. Vertical bars connect materials that are not statistically significant ($p < 0.05$).

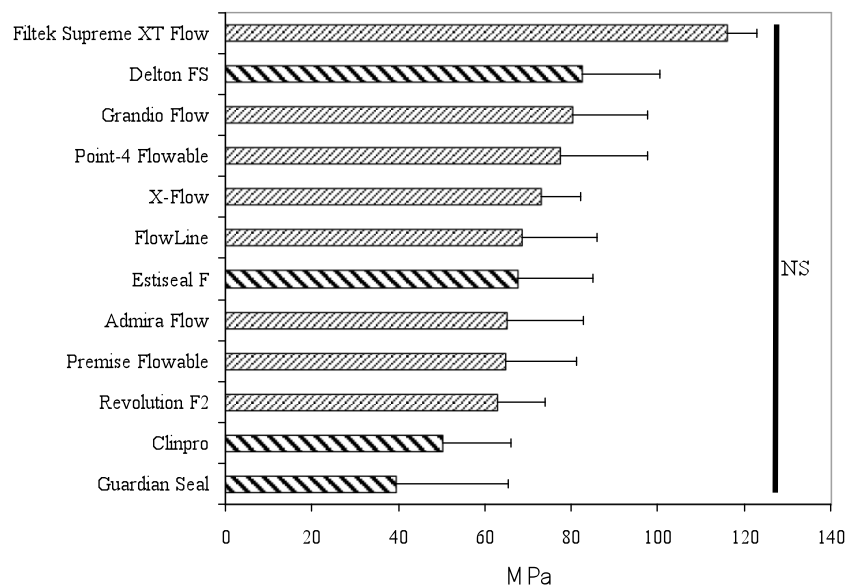


Figure 7-5: Flexural strength of the materials tested. The vertical bar connects the materials that are not statistically significant ($p < 0.05$).

The results of Vickers microhardness are shown in Figure 6. They ranged for the flowable resin composites from 15.8 VHN for the Revolution Formula 2 to 59.9 VHN for the Grandio Flow. For the pit and fissure sealants, they varied from 8.8 VHN for the Guardian Seal to 28.5 VHN for the Delton FS⁺.

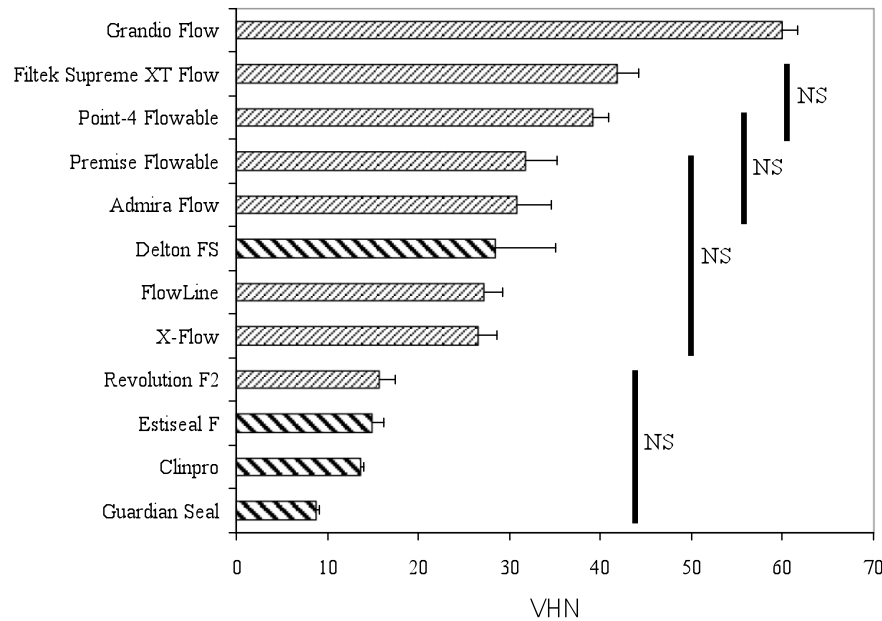


Figure 7-6: Vickers microhardness of the materials tested. Materials that are not statistically significant ($p < 0.05$) are connected by vertical bars.

3.3. Rheological properties

3.3.1. Flowable resin composites

The complex viscosities versus frequency of the flowable resin composites tested are presented in Figure 7. They all dramatically decreased as frequency increased, showing a strong non-Newtonian behavior. There is no hint of a Newtonian plateau even at very low frequencies. The difference in the complex viscosity of the materials tested between low and high frequencies lies between two and three decades. FlowLine has the highest viscosity at low and midrange frequencies while Filtek Supreme XT Flow shows the highest viscosity at high frequencies. Grandio Flow shows the lowest viscosity at low frequencies while Admira Flow has the lowest complex viscosity at midrange and high frequencies. However, Revolution Formula 2 shows the lowest viscosity at very high frequencies.

Figure 8 presents the storage moduli of the flowable resin composites. They all increase as the frequency increases. FlowLine has the highest storage shear modulus except at very high frequencies where Filtek Supreme XT Flow has the highest. Admira Flow shows the lowest storage modulus at high and midrange frequencies while Grandio Flow has the lowest storage modulus at low frequencies.

Except for Admira Flow, Grandio Flow and X-Flow, the low slopes at low frequencies indicate huge elasticity of the materials. As for the results of viscosity measurements, no transition to terminal behavior can be observed (i.e. simple liquid flow).

For clarity purpose, results of the loss moduli and loss tangents are not presented because they do not provide any additional information.

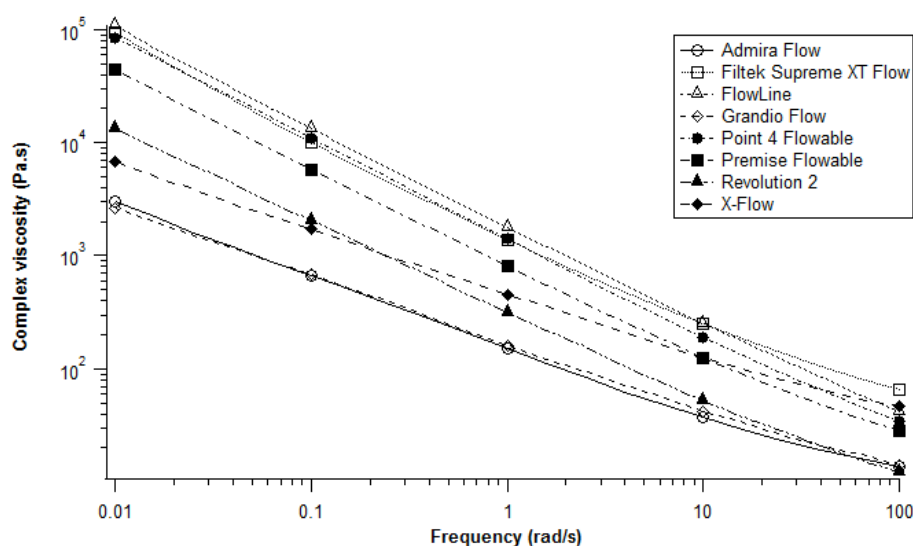


Figure 7-7: Complex viscosity (η^*) versus frequency for the flowable resin composites tested.

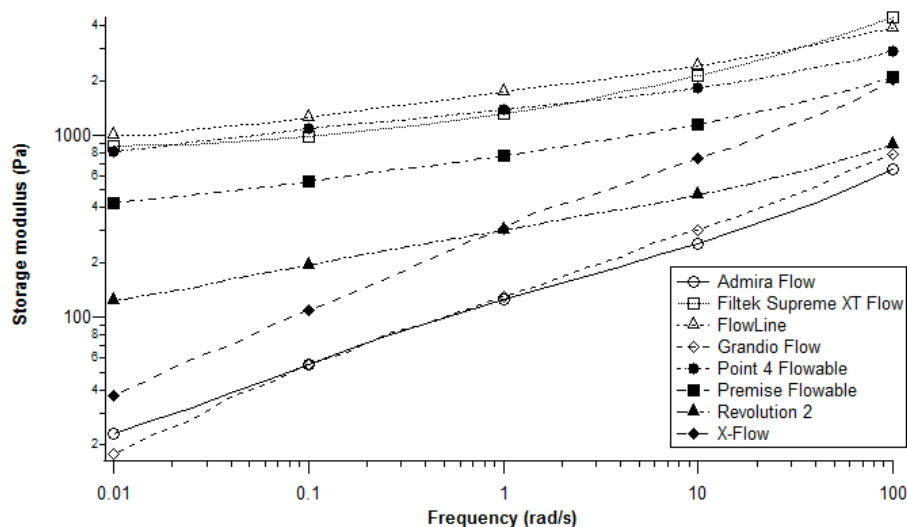


Figure 7-8: Storage modulus (G') versus frequency for the flowable resin composites tested.

3.3.2. Pit and fissure sealants

Figure 9 presents the complex viscosities versus frequency of the pit and sealant tested. They slightly decreased as the frequency increased except for Estiseal F which showed

higher variation of complex viscosity. As a consequence, they were all non-Newtonian as well. The difference in the complex viscosities between low and high frequencies lay around half a decade except for Estiseal F, which it lay at around one decade. Again, no Newtonian plateau can be observed.

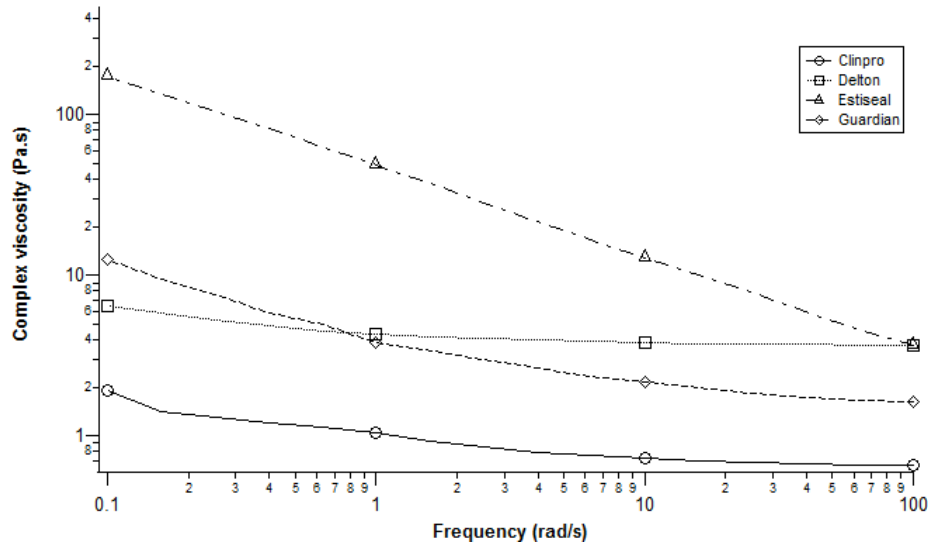


Figure 7-9: Complex viscosity (η^*) versus frequency for the pit and sealants tested (from Beun et al., 2008 [27]).

The storage moduli versus frequency are shown in Figure 10. They all increased as the frequency increased. Confirming the complex viscosity results, no sign of a transition to terminal behavior is observed.

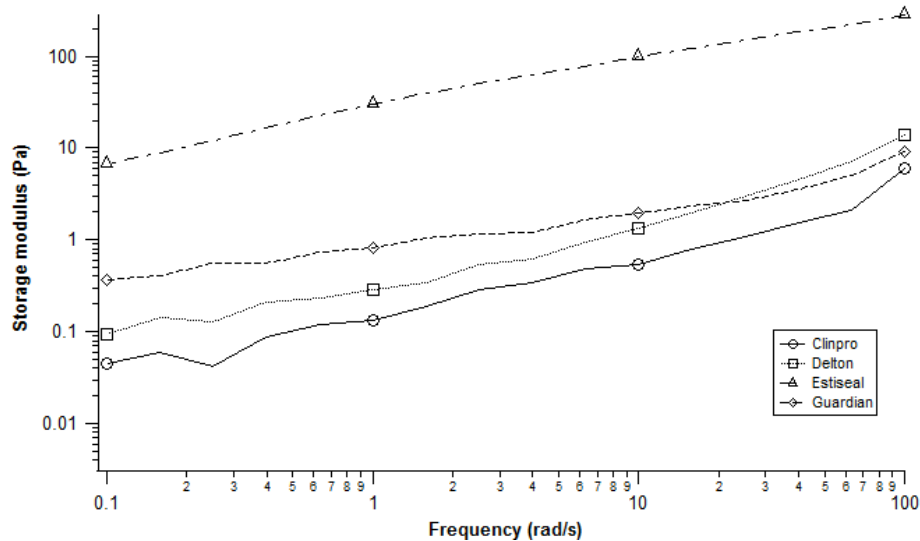


Figure 7-10: Storage modulus (G') versus frequency for the pit and fissure sealants tested (from Beun et al., 2008 [27]).

4. Discussion

The use of thermogravimetric analysis is a good method to determine the filler load in weight of dental resin composites, as demonstrated by Sabbagh et al. [25] and the values obtained with this technique are highly correlated to those obtained with the more traditional ashing in air technique. It is not surprising to see that pit and fissure sealants are poorly filled compared to flowable resin composites. Only Delton FS+ shows a filler load which is comparable to most of the flowable resin composites. It is to be noted that nano-hybrid flowable resin composites do not show higher filler load as compared to micro-hybrids, except for Grandio Flow which filler load is even higher than most of the commercially available universal hybrid resin composites as shown in a previous publication [28].

Most filler particles of both the flowable resin composites and the pit and fissure sealants are of irregular shape. More regular, spherical particles are found in Filtek Supreme XT Flow, Premise Flowable and Point-4 Flowable. It is known that a spherical shape has many advantages such as to allow an increased filler load [29] but also to enhance the fracture toughness since mechanical stresses tend to concentrate on the angles and protuberances of the particles [30]. Filtek Supreme XT Flow and Delton FS+ exhibit filler particles that are considerably larger than the other materials tested.

An optimal resin composite should mimic structural, physical and mechanical characteristics of dentin and enamel. Xu et al. [31] measured the elastic modulus of human enamel and dentin and obtained 94 GPa for the enamel while it depends significantly on tooth orientation. The dynamic and static moduli of elasticity of all the materials tested in this study are of course by far lower than that value. On the other hand, it is most probably of minor importance in the case of pit and fissure sealing since it has been shown by Dejak et al. [32] that the pits and fissures of occlusal surfaces do not encounter much stresses during clenching. In that case, a good resistance to wear is certainly more important. Vickers microhardness is, from the properties tested, certainly the one that gives the best indication of wear resistance. Grandio Flow exhibits the highest value, followed respectively by Filtek Supreme XT Flow, Point-4 Flowable and Premise Flowable. Except for Point-4, those materials all contain nano-particles. A second group of materials which show lower Vickers microhardness is formed by most of the micro-hybrid flowable composites and the Delton FS+ which microhardness is even higher than some flowable resin composites (FlowLine, X-Flow and Revolution Formula 2). A third group, formed by Revolution Formula 2 and the other pit and fissure sealants tested, show very poor microhardness. Globally, although no

strong correlation between filler load and Vickers microhardness could be made, materials which have the highest filler load show the highest microhardness while those which have the lowest filler load show the lowest microhardness.

In the case of enlarged pit and fissure sealing, the mechanical properties of the material used become more important since material can be placed up to areas that encounter mechanical stresses during clenching. In that particular situation, it appears clear from the results above that flowable resin composites have by far better elastic moduli than the pit and fissure sealants tested. As for the microhardness results, the group with the highest dynamic and static moduli of elasticity is formed by the nanofilled resin composites and the Point-4 Flowable. A second group which shows midrange results is formed by most of the micro-hybrid composites and the Delton FS+. The third group which shows the lowest moduli of elasticity includes the other pit and fissure sealants and the Revolution Formula 2.

The measurement of the flexural strength was not a discriminating factor in this study. Indeed, all the materials tested show non significantly different values. This is in accordance with a previous publication [28].

All the materials tested in this study, flowable resin composites as well as pit and fissure sealants, are viscoelastic materials. They are all non-Newtonian and show a shear thinning behavior, i.e. their complex viscosity decreases as the frequency increases.

For the flowable resin composites, two groups can be observed from the results of the rheological measurements. The first one, including Filtek Supreme XT Flow, FlowLine, Point-4 Flowable and Premise Flowable has higher viscosities and storage moduli than the others. In addition, the slope of their storage moduli at low frequencies is very close to the horizontal which indicates a very strong elasticity and thus a very strong solid-like behavior at rest. The second group, including Admira Flow, Grandio Flow and X-Flow, shows materials that have a lower complex viscosity than the previous one. In addition, their storage moduli at low frequencies show higher slopes, which is an indication of less solid-like behavior than for the materials included in the first group. Revolution Formula 2 has a different behavior than the materials cited above. From its complex viscosity at low frequencies and the slope of its storage modulus which is close to the horizontal, it could be associated with the materials included in the first group. But at higher frequencies, its rheological behavior is quite similar to the materials belonging to the second group.

Clinically, it means that a material that belongs to the second group has a better ability to flow by itself in small cavities and fissures than the composites included in the first

group, which, in the case of pit and fissure sealing, can lead to a better application of the material.

No correlation could be made between the filler load and the rheological behavior of the flowable resin composites. This is in accordance with the results obtained in a previous publication [26]. The rheological behavior of these materials is probably much more linked to the type of filler and surface treatment used than to the amount of filler included. From our results, Grandio Flow has the highest filler load (77.8 %) but shows the lowest viscosity at low frequencies coupled with the lowest storage modulus and a high slope, which indicates a low solid-like behavior at rest and thus a higher ability to flow by than the other composites tested.

The pit and fissure sealants tested are very low viscosity materials. Nevertheless, there are signs of elastic behavior at low frequencies but it can easily be assumed that their internal structure is not strong enough to counteract gravity and, by the way, to induce any solid-like behavior at rest and prevent creep flow. Again, no correlation could be made between their filler load and their rheological behavior.

As a conclusion and from our results, since preventive pit and fissure sealing does not seem to require materials with high mechanical properties, the use of materials specifically designed for that purpose looks totally adequate. On the other hand, if pits and fissures need to be enlarged for some reason, materials with higher mechanical properties are required and, so far, flowable resin composites are much better than pit and fissure sealants. The term “flowable” is unfortunately vague and for this specific indication, a material with a low elastic behavior at low frequencies is preferred for its ability to flow by itself. But rheology is not the only factor that influences the ability of the material to flow into small areas. Indeed, the surface tension after etching but also the adhesive system used can influence positively or negatively the quality of the sealing obtained.

5. Bullet points

5.1. What this paper adds

This study compares the mechanical and rheological performances of resin-based pit and fissure sealants and flowable resin composites.

Pit and fissure sealants seem adequate for preventive pit and fissure sealing. For enlarged pit and fissures, the use of a flowable resin composite with low elasticity at low frequency looks more appropriate from a mechanical point of view.

5.2. *Why this paper is important for paediatric dentistry*

This study shows that specifically designed pit and fissure sealants and flowable resin composites have very different mechanical properties and rheological behavior and thus different clinical performances and indications.

6. *Acknowledgements*

The authors would like to thank Thérèse Glorieux and Jean-Jacques Biebuyck for their technical help.

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8. MECHANICAL PROPERTIES OF EXPERIMENTAL AND COMMERCIALY AVAILABLE RESIN COMPOSITES AS A FUNCTION OF TIME BETWEEN HANDLING AND CURING

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ABSTRACT

Objectives: The purpose of this study was to investigate whether mechanical properties of resin composites are influenced by the delay between handling and polymerization.

Methods: One experimental and six commercially available flowable resin composites (Admira Flow, Filetk Supreme XT Flow, Grandio Flow, Premise Flowable, Revolution formula 2 and X-Flow) were tested. Materials were destructured by high shear flow and were then polymerized respecting different times of rest. Dynamic moduli of elasticity were measured and the morphology, dispersion and weight content were determined using transmission electron microscopy (TEM) and thermogravimetric analysis (TGA), respectively.

Results: Nanofiller-containing materials did not show any significant evolution of their dynamic moduli as a function of time. To the contrary, microhybrid materials showed a significant increase of their dynamic moduli as a function of time between destructure and curing. No correlation was found between the evolution of the dynamic moduli and the filler weight content.

Significance: Within the limitations of this study, there is a significant influence of the delay between handling and curing on the dynamic modulus of elasticity of microhybrid composites, which could have an influence on the final performances of restorations.

KEYWORDS

Resin composites, flowable, mechanical properties, filler particles, polymerizations

1. Introduction

Nowadays, resin composites restorations are by far more popular than silver amalgams in the field of restorative dentistry. Indeed, many efforts at improving their physical, mechanical and aesthetic properties have been undertaken since the very first dental resin composites were developed [1] and recently commercialized resin composites show very good clinical performances. A lot of studies are conducted on the development of new monomers [1, 2, 3], new filler particles and surface treatments [1, 4, 5], new photoinitiation systems and many other fundamental topics that contribute to improve the properties of these materials and, as a consequence, the success rate of resin composite restorations.

The influence of many clinical scenarios on the mechanical and physical properties of resin composites has been widely investigated [6, 7]. These properties may vary according to many factors. Some of them are obvious: the amount of filler particles, the particle size and silanation [8, 9, 10, 11] or the quality of the organic matrix and especially the degree of conversion and the crosslink density of the organic matrix [12, 13, 14]. But only very poor information is available on the possible influence of the handling procedures themselves.

Resin composites are, from the physicist's point of view, highly filled suspensions of inorganic particles in an organic matrix which gives these materials viscoelasticity, i.e. they have both liquid-like and solid-like behaviors, even in an uncured state. Previous studies have shown that both experimental and commercially available flowable formulations exhibit complex rheological properties and particularly shear-thinning (i.e. the viscosity decreases as the shear rate increases) and thixotropy (i.e. the viscosity depends on the time) [15, 16], which are mainly due to the presence of filler particles. This last peculiarity is explained by a strong internal structure that is destroyed when composites are submitted to flow [17]. As a consequence, there is a dramatic decrease of the viscosity of resin composites just after they have been manipulated and the recovery of the initial viscosity, which is linked to the recovery of the internal structure, may take up to two hours for commercially available materials [15]. But because in clinical conditions resin composites are polymerized just after handling, they are frozen in a state that is, from the rheological point of view, far from internal equilibrium. Since it has huge repercussions on their rheological behavior, the question can legitimately be asked if it also has an influence on other properties of cured composites and especially on the mechanical properties.

The objective of the present study was to investigate whether mechanical properties of resin composites are influenced by the delay between handling and polymerization, i.e. by

the time during which they may re-structure after destructure. One experimental and six commercially available flowable resin composites were tested. They were submitted to high shear flow in order to destroy their internal structure and were cured either immediately after flow or after various time delays. The dynamic modulus of elasticity was then measured. The spatial organization of the filler particles was investigated with transmission electron microscopy (TEM) and the filler load was determined by thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Resin composites

2.1.1. Experimental resin composite

An experimental resin composite was prepared using a Bis-GMA/TEGDMA 50/50 mixture (w/w) as the organic matrix. It was then filled at 60 wt% with two types of filler particles: silanized dental glass as macrofiller (with an average diameter of 1 μm) and partially hydrophobic silica as microfiller (with an average diameter of 0.1 μm) at respectively 55/5 wt% of the total weight of the final composite. This composition was chosen to reproduce an average flowable resin composite.

2.1.2. Commercially available resin composites

Six commercially available flowable resin composites (one ormocer, two nanohybrids, one nanofilled and two microhybrids) were tested in this study. They are listed in Table 1.

Material	Manufacturer	Type	Shade	Batch
Admira Flow	Voco (Cuxhaven, Germany)	Ormocer	A3	680934
Filtek Supreme XT Flow	3M-ESPE (St.Paul, MN, USA)	Nanofilled	A3	680934
Grandio Flow	Voco (Cuxhaven, Germany)	Nanohybrid	A3	671609
Premise Flowable	Kerr (Orange, CA, USA)	Nanohybrid	A3	06-124102
Revolution F2	Kerr (Orange, CA, USA)	Microhybrid	A3	06-173
X-Flow	Dentsply-De Trey (Konstanz, Germany)	Microhybrid	A3	0502000636

Table 8-1: List of the materials tested.

2.2. Dynamic moduli of elasticity

Five specimens of each material were prepared in moulds of 25 mm x 2 mm x 2 mm as specified in the ISO specification 4049 [18]. Samples were light-cured using two

conventional curing devices (XL 3000, 3M-ESPE, St Paul, MN, USA, 650 mW/cm²) by overlapping irradiations for a total of 60 s on both sides. In order to investigate the influence of the internal structure on the dynamic modulus of elasticity, all materials were destructured when placed in the moulds by flowing through a syringe's application tip to provide sufficient shear. Several groups were then made by waiting a specified time between placement in the moulds and photopolymerization to allow materials to partially recover their internal structure. For the experimental composite, four groups were made with the following delays between placement and curing: 0 min, 3 min, 30 min and 90 min. For the commercially available materials, three groups were made with the following delays: 0 min, 3 min and 120 min. Delays were determined according to thixotropy curves available in previous publications [15, 16] for both experimental and commercially available materials. Five samples of each group were prepared. Specimens were stored for 7 days in water at 37°C before measurement.

The dynamic modulus of elasticity was measured non-destructively by the impulse excitation technique (Braem *et al.*, 1986) [19]. Each sample was set in flexural vibration by a light mechanical impulse. The signal produced was captured via a microphone placed underneath the sample by a special signal analyzer, the Grindosonic (Lemmens Elektronics, Haasrode, Belgium). Modulus of elasticity (GPa) was calculated from the fundamental frequency, the mass, the width, the length and the thickness of the bar as follows:

$$E_d = 0.9465 \frac{mf_t^2}{b} \frac{L^3}{t^3} T_1$$

where m is the mass of the bar, b the width of the bar, L the length of the bar, t the thickness of the bar, f_t the fundamental frequency of the bar in flexion – which appears on the screen of the machine -, and T_1 a correction factor for fundamental flexural mode to account for finite thickness of the bar, Poisson's ratio and other constants. Poisson's ratio is the ratio of transverse strain (contraction) to axial strain (elongation) in a uniaxial tensile test [20]. When applied to dental resin composites, its value lies around 0.30 [21], which value has been taken as the mean value for all the materials tested in this study.

2.3. Characterization of the inorganic fraction

2.3.1. Weight percentage of fillers

The weight percentage of fillers was determined using Thermogravimetric Analysis (TGA/SDTA861^e, Mettler-Toledo, Greinfensee, Switzerland). It evaluated weight changes as

a function of time and temperature during a thermal program ranging from 30°C to 900°C at the rate of 10°C/min in normal atmosphere followed by air cooling to room temperature. The calculated ratio between the final weight of the sample and its nominal weight is assigned to the inorganic fraction. Three samples of each material were analyzed.

2.3.2. Fillers dispersion and morphology by TEM

The fillers dispersion in the organic matrix and morphology was determined using TEM. A specimen of each material tested was prepared in a mould of 25 mm x 2 mm x 2 mm. The samples were light-cured using two conventional curing devices (XL 3000, 3M-ESPE, St Paul, MN, USA, 650 mW/cm²) by overlapping irradiations for a total of 60 s on both sides. Slices were then made using an ultra-microtome (Ultracut S, Reichert, Depew, NY, USA) equipped with a diamond knife (Diamond Knife Ultra 35°, Diatome, Biel, Switzerland). Micrographs were obtained using TEM (LEO922, Carl Zeiss SMT AG, Oberkochen, Germany) with an acceleration tension of 200 keV at 12,500 x magnification, except for Grandio Flow which is at 20,000 x magnification for clarity purpose.

2.4. Statistical analysis

Statistical analysis for the values of dynamic moduli and percentage of fillers by weight was made using a one-way ANOVA and Scheffe's multi-comparison tests at $p < 0.05$ level.

3. Results

3.1. Dynamic moduli of elasticity

Mean values and standard deviations of the dynamic moduli of elasticity of the experimental resin composite tested are presented in Figure 1. Values varied between 8.63 GPa for the 0 min group and 9.60 GPa for the 90 min group. The 0 min group was significantly different from the 90 min group ($p < 0.05$).

For the Admira Flow, values are presented in Figure 2. The 0 min group, at 6.43 GPa, was significantly lower ($p < 0.05$) than the 3 min and the 120 min groups, respectively at 8.33 and 8.07 GPa.

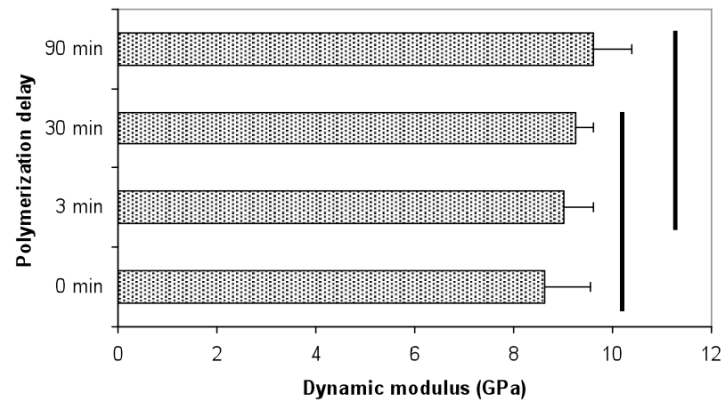


Figure 8-1: Dynamic moduli of elasticity according to the delay between handling and curing for the experimental resin composite tested. Vertical bars connect groups that are not statistically significant ($p < 0.05$).

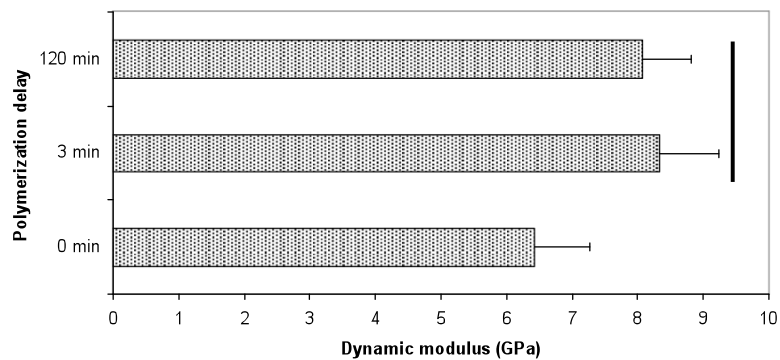


Figure 8-2: Dynamic moduli of elasticity according to the delay between handling and curing for the Admira Flow. Groups that are not statistically significant ($p < 0.05$) are connected by the vertical bar.

Values of the dynamic moduli of elasticity of the Filtek Supreme XT Flow are shown in Figure 3. The three groups were not statistically different ($p < 0.05$). The same observation was made for the Grandio Flow and the Premise Flowable. The values of their dynamic moduli are presented respectively in Figure 4 and Figure 5.

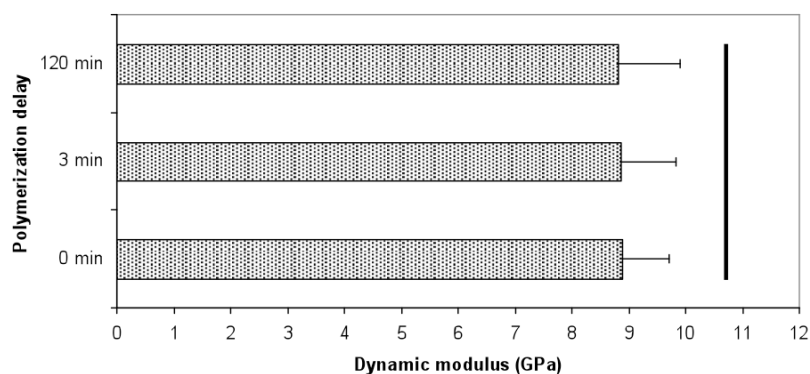


Figure 8-3: Dynamic moduli of elasticity according to the delay between handling and curing for the Filtek Supreme XT Flow. The vertical bar connects groups that are not statistically significant ($p < 0.05$).

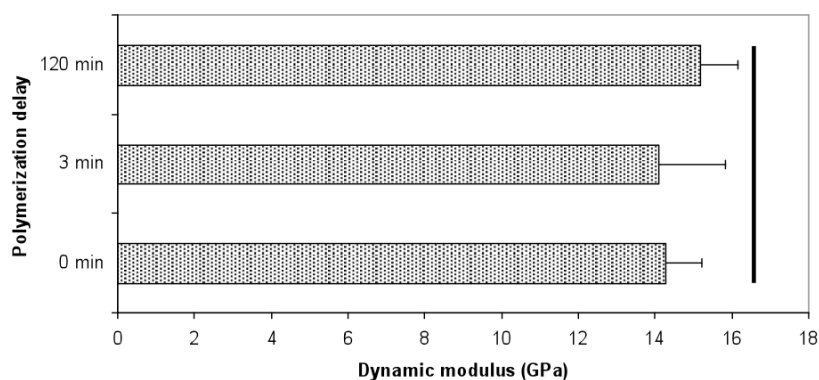


Figure 8-4: Dynamic moduli of elasticity according to the delay between handling and curing for the Grandio Flow. Groups that are not statistically significant ($p < 0.05$) are connected by the vertical bar.

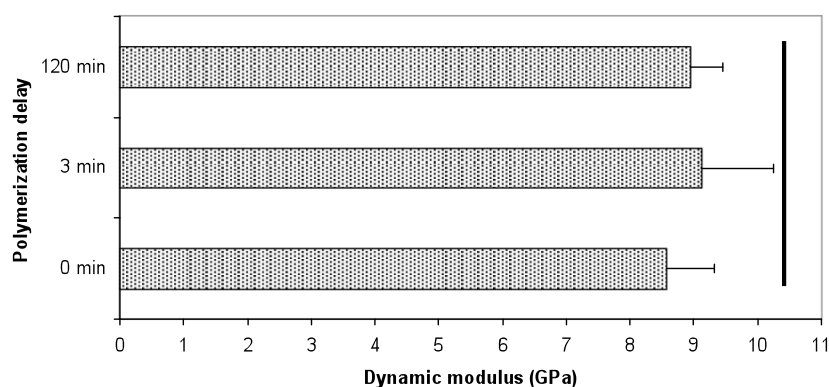


Figure 8-5: Dynamic moduli of elasticity according to the delay between handling and curing for the Premise Flowable. The vertical bar connects groups that are not statistically significant ($p < 0.05$).

For the Revolution Formula 2, the 0 min group (4.01 GPa) was significantly lower than both the 3 min (6.19 GPa) and the 120 min (6.62 GPa) groups at $p < 0.05$. Values are shown in Figure 6.

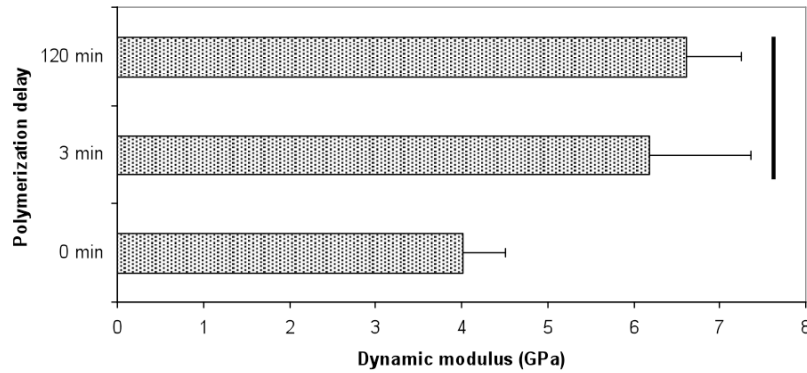


Figure 8-6: Dynamic moduli of elasticity according to the delay between handling and curing for the Revolution Formula 2. Groups that are not statistically significant ($p < 0.05$) are connected by the vertical bar.

The dynamic moduli of elasticity of the X-Flow are presented in Figure 7. The 120 min group (9.72 GPa) was significantly higher than the 0 min (7.10 GPa) and the 3 min (8.28 GPa) groups ($p < 0.05$).

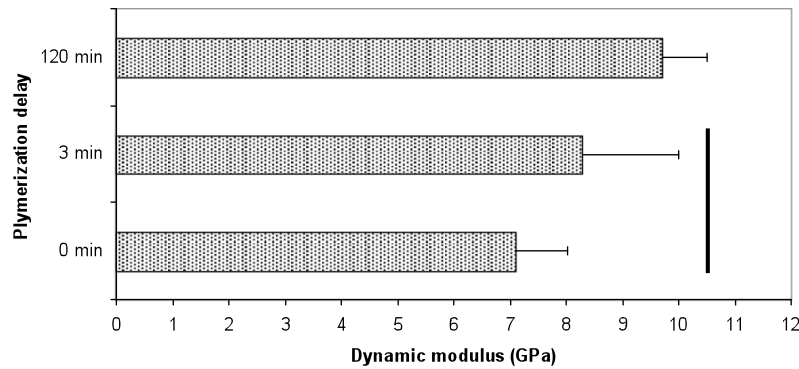


Figure 8-7: Dynamic moduli of elasticity according to the delay between handling and curing for the X-Flow. The vertical bar connects groups that are not statistically significant ($p < 0.05$).

3.2. Characterization of the inorganic fraction

3.2.1. Weight percentage of fillers

The mean values and standard deviations of the weight percentage of fillers of the materials tested are shown in Figure 8. They ranged from 45.01 % for the Revolution Formula

2 to 77.78 % for the Grandio Flow. The experimental resin composite showed 59.63 % of filler by weight.

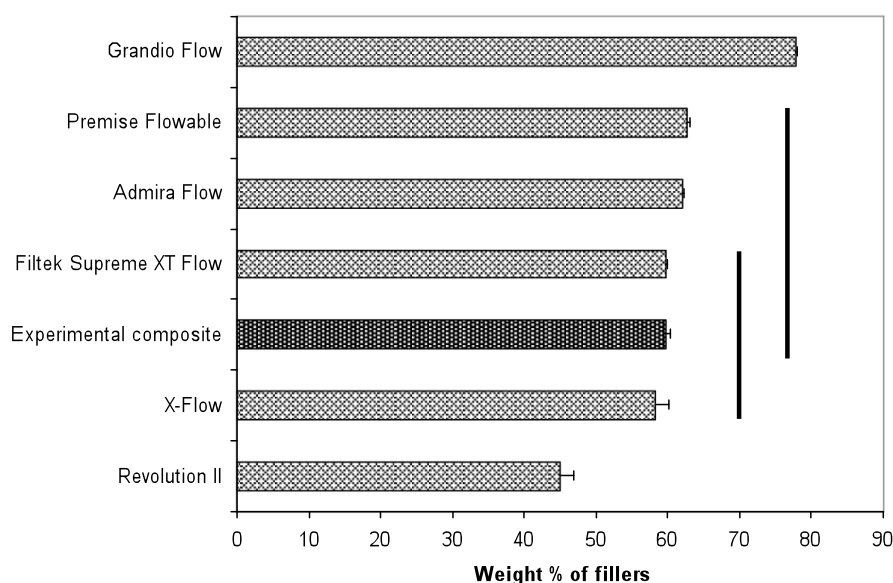


Figure 8-8: Mean values and standard deviations of the percentage of filler by weight of the composites determined by thermogravimetric analysis. Vertical bars connect materials that are not statistically significant ($p < 0.05$).

3.2.2. Filler dispersion by TEM

The TEM microphotograph of the experimental resin composite tested is presented in Figure 9. It showed irregular macrofiller and a network of fumed silica agglomerates.

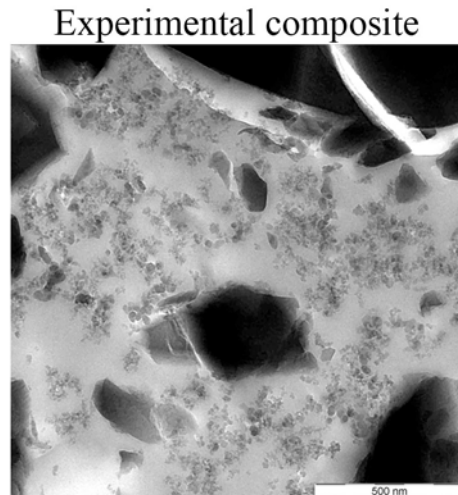


Figure 8-9: Dispersion of the fillers by transmission electron microscopy at 12,500 x magnification of the experimental resin composite tested.

Figure 10 presents the TEM microphotographs of the commercially available composites tested. They all showed irregular macrofiller, except for the Filtek Supreme XT Flow which had rather spherical particles. In addition, theOrmocer tested (Admira Flow) presented a network of fumed silica agglomerates. Filek Supreme XT Flow, Grandio Flow and Premise Flowable all had isolated nanoparticles. Revolution Formula 2 and X-Flow both showed fumed silica aggregates as microfiller, but at lower concentrations than for the Admira Flow and the Grandio Flow. In addition, Filtek Supreme XT, Grandio Flow, Premise Flowable and Revolution Formula 2 showed spherically shaped, translucent particles of around 100 nm to 200 nm.

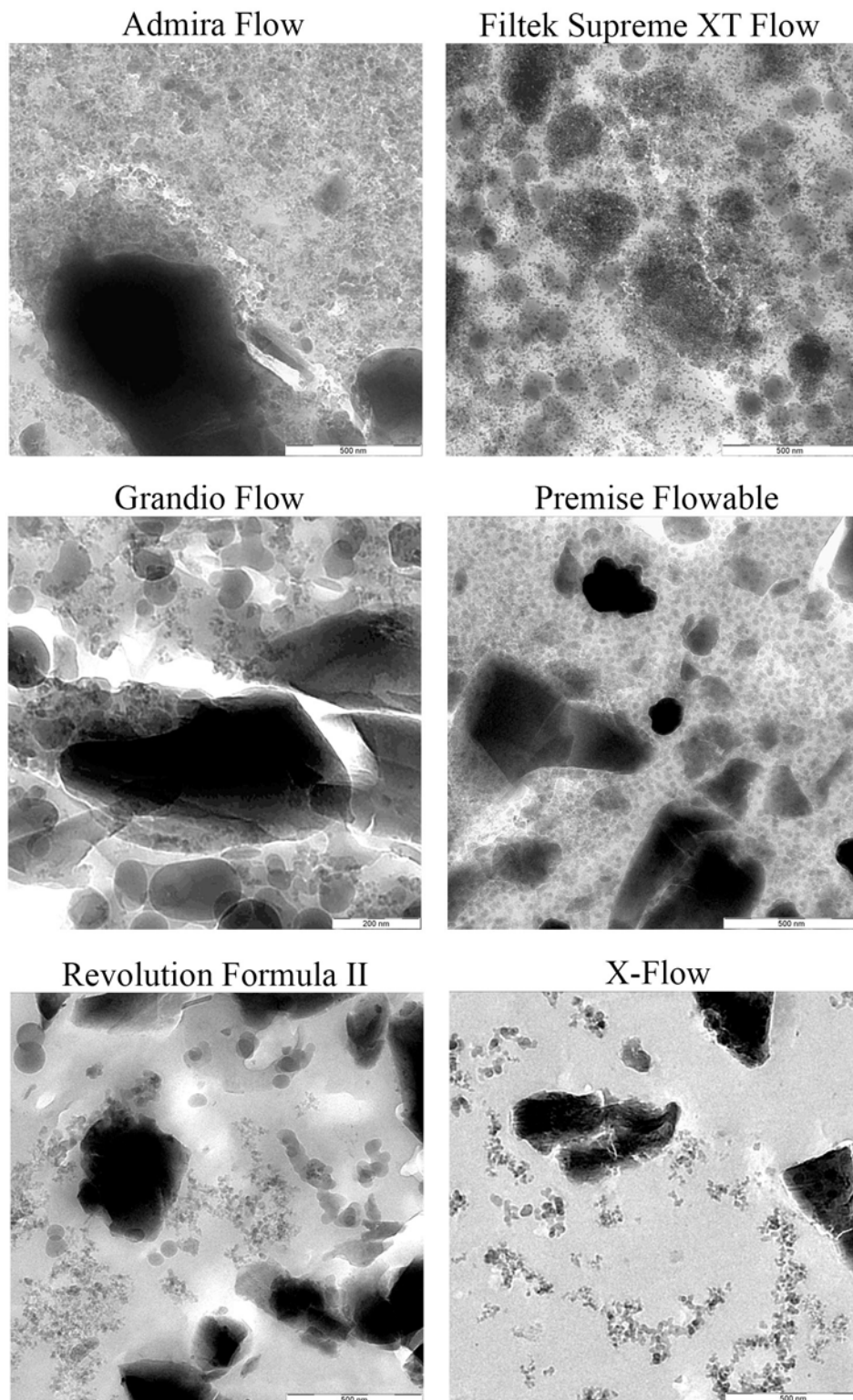


Figure 8-10: Dispersion of the fillers by transmission electron microscopy at 12,500 x magnification of the commercially available resin composites tested, except for Grandio Flow which is at 20,000 x magnification for clarity purpose.

4. Discussion

The dynamic modulus of elasticity of the experimental resin composite tested in this study increases as the delay between handling and polymerization increases. Although this is not significant for all groups, there is a statistically significant increase of around 1 GPa in dynamic modulus between the group that is polymerized immediately after destructureation and the group for which a delay of 120 minutes was observed before curing (with values of 8.63 GPa and 9.6 GPa, respectively).

For the commercially available resin composites, three classes of materials may be distinguished regarding the evolution of the dynamic modulus as a function of time between handling and polymerization. The first class, including the Admira Flow and the Revolution Formula 2, shows a significant difference for the group for which no delay was respected as compared with the two other groups, with important differences in the values of dynamic moduli. For the Revolution Formula 2, the dynamic modulus for the 120 minutes groups is more than 150 % that of the 0 minute group (at 6.62 GPa and 4.01 GPa, respectively). The second class, including only the X-Flow, exhibits a significant difference between the 120 minutes' group and both the others. Finally, the third class of materials, including the Filtek Supreme XT Flow, the Grandio Flow and the Premise Flowable, does not exhibit statistically significant differences among the different groups tested. The values that were measured for the Filtek Supreme XT flow are surprisingly stable as compared to those obtained for the other materials tested, varying only from 8.82 GPa for the 120 minutes groups to 8.89 GPa for the 0 minute group.

The measurement of the filler load in weight by the use of thermogravimetric analysis is a valid method [22] and the values obtained are highly correlated with the more traditional ashing in air technique. From the experimental formulation and the six commercially available materials tested, five have a filler load that lies between 58 % and 63 %. Only the Revolution Formula 2's filler load is lower, at around 45 %, and the Grandio Flow's is higher, at around 78 %. It is to be noted that from the three materials that contain nanofillers, only Grandio Flow has a significantly higher filler load than all the microhybrids tested. These results validate the experimental formulation tested as a mean flowable composite in terms of total filler content in weight.

Regarding the filler dispersion and morphology, all the materials tested show irregularly shaped macrofiller, except for the Filtek Supreme XT Flow which exhibits more spherically shaped particles that are referred as silica-zirconium nanoclusters by the

manufacturer [23] rather than the more traditional dental glass particles used in the other formulations. Concerning the other particles, theOrmocer (Admira Flow), the two microhybrids (Revolution Formula 2 and X-Flow) and the experimental composite show fumed silica aggregates as microfiller, however at different concentrations. The nanofilled (Filtek Supreme XT flow) and the two nanohybrids (Grandio Flow and Premise Flowable) all exhibit isolated nanofiller. The spherically shaped, translucent particles of around 100 nm to 200 nm contained in the Filtek Supreme XT, Grandio Flow, Premise Flowable and Revolution Formula 2 are most probably titanium dioxide that is traditionally used as an opacifier. Again, the observations that can be made from the TEM microphotographs validate the experimental formulation tested as a mean microhybrid flowable resin composite.

The macrofiller has a huge positive influence on the mechanical properties as well as on the polymerization shrinkage of resin composites. But, as it was developed in a previous publication [16], it has only minor influence on the rheological properties of materials: the Newtonian viscosity is increased but only a very slight shear-thinning behavior appears and no noticeable thixotropic behavior may be observed. The rheological behavior of composites is much more influenced by the sub-micronic particles, whose presence, even in very small amounts, leads to the appearance of huge shear-thinning and thixotropic behaviors. The internal structure is thus mainly linked to sub-micronic particles instead of macrofiller. From these observations it is clear that it is not worth trying to correlate the evolution of the dynamic modulus as a function of time to the characteristics of the macrofiller. But some observations can be made from the microfiller and the nanofiller. Indeed, according to the classification made on the basis of the evolution of the dynamic moduli, the first class materials (Admira Flow and Revolution Formula 2) contain aggregates of fumed silica that is typically found in microhybrid materials and show significant increase of their dynamic modulus between the 0 minute and the 3 minutes groups. The X-Flow, that constitutes the third class, shows similar microfiller but at lower concentration and also exhibits a significant increase of its dynamic modulus as a function of time. The difference with the first class materials is that significant increase does not occur in the first minutes after handling but after a longer time. The second class of materials, that includes the three nanofiller-containing composites, does not show any significant change in dynamic modulus. The experimental composite tested may be placed in between the first and the third class of materials in terms of fillers composition and dispersion as well as in terms of evolution of dynamic modulus. Thus, within the limitations of this study, all the resin composites that show a variation of their dynamic modulus over time contain fumed silica aggregates that are partially hydrophobic.

Those that do not show any significant variation in their dynamic modulus contain isolated nanoparticles that are known to have reduced particles interaction by the way of an optimal silanation [1, 23]. A previous publication showed that there is no noticeable difference in the spatial organization of the fillers between destructured and non-destructured materials [16]. A possible explanation of the internal structure of resin composite can be made by the presence of indirect interactions between filler particles through the organic fraction. Indeed, as the specific surface of silica is huge and because fumed silica aggregates are only partially silanated, a very important part of the monomers interacts with the fillers surface. Interaction probably results in a layer that surrounds the particles where the monomers mobility is significantly reduced by indirect chemical interactions with the fillers. This has been widely described in dispersions of silica in rubbers, where the thickness of such a layer is directly influence by both the specific surface of the filler and the nature and quantity of surface treatment [24, 25]. As nanofillers present reduced interactions, this layer may be significantly reduced and, as a consequence, the internal structure of nanofiller-containing materials may be weaker or less influenced by the time, even though it was shown in a previous publication that Grandio Flow, even though no significant evolution of its dynamic modulus versus time could be observed, also shows thixotropy [15].

No correlation could be made between the evolution of the dynamic moduli of elasticity of the materials tested and their filler weight content. This is not surprising as there is no correlation between rheological properties and filler load neither. It is most probably the type of filler that influences the evolution of the mechanical properties as a function of time than the amount of it, as it is more the type of filler that influences the thixotropic behavior than the amount of it [16]. However, evolution of the mechanical properties over time does not seem to be directly linked to the presence of a thixotropic behavior so far.

Further studies are required to fully understand the exact nature of the interactions between both the filler particles and the organic matrix in order to explain the phenomenon that was observed in this work. Hence, the clinical relevance of these variations in dynamic moduli over time should be investigated.

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9. APPENDICES

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