DENTAL PRODUCTS REPORT
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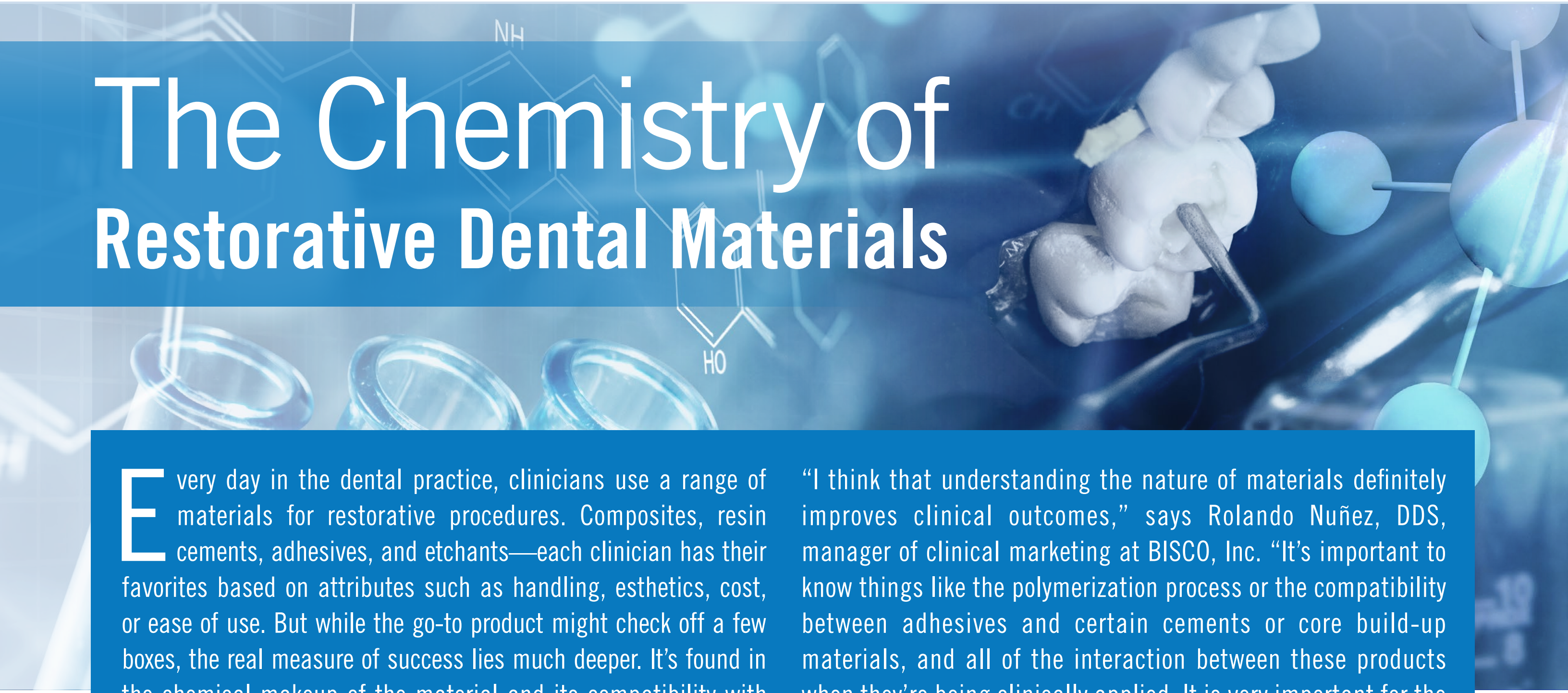

The Chemistry of Restorative Dental Materials

Every day in the dental practice, clinicians use a range of materials for restorative procedures. Composites, resin cements, adhesives, and etchants—each clinician has their favorites based on attributes such as handling, esthetics, cost, or ease of use. But while the go-to product might check off a few boxes, the real measure of success lies much deeper. It's found in the chemical makeup of the material and its compatibility with other materials.

While it may seem like an unnecessary deep dive, understanding the chemical nature of the restorative materials in the dental practice can have a big impact on clinical success. It will improve the way a material performs in a clinician's hands, and give a patient better, longer-lasting results.

"I think that understanding the nature of materials definitely improves clinical outcomes," says Rolando Nuñez, DDS, manager of clinical marketing at BISCO, Inc. "It's important to know things like the polymerization process or the compatibility between adhesives and certain cements or core build-up materials, and all of the interaction between these products when they're being clinically applied. It is very important for the clinician to understand how these things happen, because the clinician being well aware of the chemistry will provide a good clinical outcome."

In short, to understand what makes a restoration successful, clinicians first need to understand the materials at their most basic level.

The Materials in Play

While there is a plethora of different materials used in dentistry, they can generally be categorized into 3 groups: ceramics, metals, and polymers.

Ceramics include materials such as glass, lithium disilicate, zirconia, and feldspathic porcelain. These materials are generally stiff, brittle, and heat- and electrical-insulating, says Nathaniel Lawson, DMD, director of biomaterials at the University of Alabama at Birmingham School of Dentistry. "Ceramics are composed of ionic and covalent bonds," he explains, "and will typically fail when cracks split planes of atoms apart."

In comparison, metals, such as amalgam, gold, or cobalt-chromium frameworks, are more heat- and electrical-conducting, as well as more malleable. This is largely due to the fact that metals allow plastic flow when deformed, allowing the planes of atoms to slide past each other without separating.

Impression materials and denture acrylic fall under the polymer category. Depending on their chemical structure, these materials can have a range of properties, and are formed by chains of monomers.

Over the years, composite materials composed of a combination of the aforementioned categories have become prevalent. Examples such as resin cements and dental composites, and glass ionomers, contain a polymer matrix with reinforcing ceramic or metal particles.

"To make a dental composite, manufacturers typically start out by mixing together various structural and functional organic resins, all with different physical and chemical properties," explains Gary Alex, DMD. "Into this 'resin soup,' various inorganic—or in some cases, organic—filler particles are added and blended."

The Building Blocks of Composite Materials

The most fundamental component of the "resin soup" in composite materials is the resin itself. Based on methacrylate chemistry, the majority of composite materials available today use dimethacrylates such as Bis-GMA (bisphenol A-glycidyl methacrylate) or UDMA (urethane dimethacrylate) as primary resins. Dimethacrylates have 2 methacrylate ends separated by a long chain. The long center chain lengthens the molecule, which can help reduce polymerization shrinkage, while the 2 bonding ends create chain formation and cross linking.

Dr Lawson points out that this formula differs critically from that of poly-methyl methacrylate (PMMA), which is used in provisional crown materials and denture base. PMMA is composed of many units of the methyl methacrylate (MMA) monomer. "When the MMA monomers join together during polymerization, the intermolecular distance between monomers decreases," Dr Lawson says. "This causes shrinkage of the material that would not be clinically acceptable if PMMA was used for a direct restoration. Therefore, different types of dimethacrylate resins were formulated for direct restorative materials."

In addition to the resin, composites contain reinforcing fillers. To link the resin and fillers, silane is used. Silane is a molecule that contains a silanol group on one end and a methacrylate on the other. The silanol group bonds to glass, while the methacrylate bonds to the resin matrix, forming a seal between the resin and filler particles.

Typically, filler particles are crushed silicate glass. Filler particles are a variety of sizes and shapes, which can affect mechanical properties and esthetics. Generally speaking, materials with larger particles have better physical properties, but poorer esthetics. At over 100 µm, early fillers were quite large, which left areas of exposed resin in between the filler particles that were susceptible to wear. As a result, Dr Lawson says, the larger filler particles would "pluck" out of the resin matrix, causing roughening, dulling, and wear.

This led to the introduction of hybrid composites that added 40 nm spherical silica particles to fill the gaps between the larger particles. Monomers of lower molecular weight, such as ethylene glycol dimethacrylate or triethylene glycol dimethacrylate, reduce the viscosity of the composite to allow more filler to be incorporated.[1] Eventually technology improved, and glass fillers could be ground smaller, leading to microhybrid and nanohybrid materials. In comparison to their larger predecessors, these smaller-particle composites tend to wear and polish better.

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"The fillers in early composites were quite large, so they would provide great mechanical properties but would not allow for the product to be as esthetic as you would want," Dr Nuñez says. "Now, a lot of the fillers are at a nanoscale, so they provide better polish and better wear. And they also help in achieving good mechanical properties, so there is a huge impact of nanotechnology composite development nowadays."

Dental Composites

As with other restorative materials, dental composites are composed of a resin matrix, filler particles, and a silane coupling agent. They also include light or chemical initiators and additives to provide color and shades. Because most resin composites are based on methacrylate chemistry (and generally contain dimethacrylate molecules), in theory most materials should be compatible. But that isn't always the case, cautions Dr Nuñez.

"There is this thought that all materials are similar—or maybe even considered the same—in some categories because of how the industry categorizes things," he says. "However, they are not, because every company has its own take on how to develop a product and the type of chemistry that is in that product. When you start mixing products from different companies, this is where the clinician really needs to know the chemical interaction to make sure that the material will perform to the expectations."

Perhaps the biggest variation is apparent in the filler content of resin composites. The filler is a vital component; the particle size, nature, and concentration of the filler greatly influence the resulting formulation's properties. Dental composites are often classified by their filler type and size, and labeled either conventional, microfilled, hybrid, or nanocomposites.

While the resin gives the composite the fluidity needed to allow handling pre-cure and the flexibility to absorb stress post-cure, the filler particles satisfy many functions. Fillers help reduce post-cure polymerization stress of the composite structure, as unlike resin, they don't experience polymerization shrinkage. Their higher modulus also gives composite material more rigidity, reinforcing the composite structure and preventing cracks from occurring in the weaker resin matrix.

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Nanomaterials

To accomplish this, composites require a filler that will provide mechanical properties and esthetics. As mentioned, smaller fillers generally create better esthetics, but historically have been weaker. Now, nanoparticles are strengthening composites as well as providing increased esthetics. These nanocomposites offer increased physical properties, as more fillers can be added in when the particles are smaller. Dr Lawson likens it to filling a jar with sand versus filling it with rocks: there are far fewer air spaces when the jar is filled with sand.

"While there are some 'true' nanocomposites (meaning all the filler particles are nanoparticles or nanoclusters), most dental composites marketed as nanocomposites are in fact a mixture of larger, conventionally ground glass particles that are typically used in composite formulations blended with chemically synthesized nanoparticles," Dr Alex says. "Generically, these are called nanohybrid composites and many, if not most, dental composites today fall into this classification category."

In the truest sense, nanoparticles are built from the ground up. Unlike the traditional glass particles used in fillers that are physically ground into smaller pieces

AELITE™ AESTHETIC ENAMEL - A NANOFILLED COMPOSITE

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through a milling process, nanoparticles are created chemically, Dr Alex explains.

“Nanoparticles are created chemically, typically through a sol-gel process, whereby atoms and molecules are built up at the quantum level into larger (but still incredibly small) particles,” he says. “In this sense, the nanoparticles used in dental composites are not created physically from the top down, but chemically from the bottom up—a very different approach.”

Creating such tiny particles is what leads to esthetic improvement and highly polishable surfaces. When filler particles are smaller than the wavelength of light, it isn’t visible when a particle is lost during polishing or wear. This allows the composite to have a higher level of gloss, because irregularities can be smoothed below visible light’s wavelength.

“The potential applications of nanotechnology are vast and encompass many areas of dentistry, including improvement of composite physical and optical properties, as well as the potential to impart antimicrobial activity,” Dr Alex says. “I think it is important for dentists to understand what nanoparticles are and how they contrast to more conventional filler products.”

Polymerization

Understanding the chemical composition of a composite is also critical in polymerization. Almost all contemporary composites require a light-curing mechanism of some sort, so clinicians need to know which type of polymerization process is necessary for a specific composite and whether that process is activated by light, chemical application, or a combination of both.

“By understanding that, the clinician can also decide what bonding agent they are going to use and make sure that the bonding agent is compatible,” Dr Nuñez says. “Otherwise, you’re going to hinder the ability of the material to achieve its optimized physical property. It’s going to have a negative impact on the clinical outcome if you don’t understand the nature of the chemistry.”

Light curing activates photoinitiators (such as camphorquinone) to react with a coinitiator (such as tertiary amine) to produce a free radical and initiate resin polymerization. The most common photoinitiator used in dentistry, camphorquinone absorbs light with a wavelength of approximately 468 nm, which, Dr Lawson explains, is the reason curing lights emit blue light. Understanding wavelength absorption numbers can also be critical to curing success.

“Some alternative photoinitiators, such as those used in bleach shade composites or some bulk-fill composites, absorb light in the violet region of light,” Dr Lawson says. “Therefore, it is suggested to use curing lights with different-colored LEDs with those materials.”

Resin Cements

From a chemical composition stance, resin cements don’t differ greatly from resin composites. Typically

CHOICE™ 2 A LIGHT-CURED RESIN CEMENT

DUO-LINK UNIVERSAL™ A DUAL-CURING RESIN CEMENT

composed of diacrylate resin with 50% to 80% glass filler particles, resin cements usually contain filler particles less than 1.0 μm.[2] One key difference between resin composites and cements is that the cements have reduced filler content. Resin cements need to have variable handling and viscosity so that thin film thickness can be achieved when placing indirect restorations. To reduce the viscosity, filler is reduced. This reduction does come at a cost: Resin cements lose the benefits provided by fillers such as lowered polymerization shrinkage, wear resistance, and strength.

The fact that resin cements do incorporate some fillers however, makes them stronger than other options, such as zinc phosphate, glass ionomer, or carboxylic cements. They also have the lowest solubility of any type of available cement, making them ideal for use in the mouth.[3] This is due in part to their polymer composition, which makes them hydrophobic by nature and not soluble. Additionally, resin cement has very low water sorption, so it won't expand over time and create stress than can crack restorations.

Over the years, manufacturers have made great advances in resin cements, and numerous variations are now available for practically any bonding or cementation requirement. Resin cements are often dual-cure materials, requiring a chemical-cure mechanism of generating free radicals in conjunction with light curing. The chemical cure is usually initiated by benzoyl peroxide and amine coinitiators and is typically required because portions of the cement layer will not be exposed to light.

For cementation of thin or translucent materials where light can penetrate and activate photo-initiators, light-cure resin cements can be used. Light-cure resin cements are known to have better color stability than their dual-cure counterparts.[4] Alternatively, chemical-cure (also known as self-cure) resin cements polymerize via a chemical reaction, which can be useful when cementing in areas where light curing is challenging.

"Resin cements exist in several variants, with some designed to be used in conjunction with other materials (primers, adhesives, etc) and others as stand-alone materials," Dr Alex says. "Dual-cure, self-etching, self-priming resin cements are popular with dentists because they do not require a separate bonding agent be placed on the tooth."

However, Dr Alex cautions, dentists should be aware that the strongest bonds to tooth structure are achieved by using a resin cement in conjunction with a separate bonding agent. For example, studies show that a resin-based cement coupled with a bonding agent provides the most durable and predictable bond to tooth structure when it comes to bonding restorations on minimally retentive preparations.

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Adhesives

When it comes to adhesives, it really is all about the chemistry. Adhesive composition is influenced by its function: Because adhesives are responsible for forming a bond between the tooth structure and the

resin composite or cement, they are methacrylate-based so they can chemically bond compatibly.

"In order to develop a viable adhesive, very specific and synergistic functional and cross-linking monomers that are multifunctional in nature are required," Dr Alex says. "They must be capable of reacting with a number of different substrates, able to copolymerize with chemically compatible resin-based restoratives and cements, have some hydrophilic character, and yet at the same time be as hydrophobic as possible once polymerized to discourage hydrolysis and water sorption over time."

Typically, an adhesive's bond to the enamel is produced by integrating the cured resin into the etched enamel surface. A bond to dentin gets a little more complicated. Resin adhesive must permeate the collagen network of the dentin to form a base for adhesion. A hybrid layer—an organic interface between the dentin substrate and the adhesive resin—must be created, wherein mineral components are replaced by resin monomers to form a polymer-collagen biocomposite.[5] Dr Lawson also notes that contemporary adhesive-containing molecules, such as MDP (10-Methacryloyloxydecyl dihydrogen phosphate), may form stable salts with the calcium in tooth minerals, allowing a chemical bond.

Because adhesives need to be easily spread across a tooth preparation, they need to have a relatively low viscosity so that the film thickness when polymerized is thin enough to not interfere with the seating of indirect restorations. Adhesives that are more dilute will spread easier, and handling of particular adhesives can vary based on the brand's solvent concentration. This lower viscosity is easily attained as adhesives are typically unfilled, because they aren't designed to withstand mechanical loading. They also differ from resin cements and composites in that they nearly all contain hydroxyethyl methacrylate (HEMA). A small molecule, HEMA is hydrophilic on one end and hydrophobic on the other. This allows hydrophobic resin adhesives to infiltrate the moisture-filled collagen in the etched dentin.

"Although it possesses a necessary function, HEMA also comes with its problems," Dr Lawson says. "The hydrophilic end of HEMA attracts water, which can facilitate hydrolytic degradation of the adhesive layer bonded to dentin, or possibly water-based staining if HEMA-containing adhesive is applied to the external surface of a resin composite (ie, used to smooth the material)."

Within the adhesive family, there are many chemical differences that can affect compatibility with resin cements or composites and impact the viability of the adhesive system. These vary from manufacturer to manufacturer, and include the different types of monomers in a brand's formulation, the polymerization initiator, the solvent type and concentration, as well as pH, which can play a big role in product compatibility. Studies have found that the pH of adhesive systems can affect the polymerization and bond strength of self-cure resin materials, prevent the self-sure mechanism of dual-cure cements and build-up materials, and compromise the clinical success of the procedure.[6] In particular, self-etching adhesive systems have to walk the line between being acidic enough to effectively etch, but not so acidic that they break down the initiators necessary for the polymerization of self- and dual-cure resin cements.

"There is a direct correlation between pH and the compatibility of universal adhesives with self- and dual-cure resin cements and composites," Dr Alex says. "As

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a generalization, the more acidic the adhesive, the less compatible it is with the self-cure mode of dual-cure resin-based materials."

This, he says, is primarily due to the acid deactivating the aromatic tertiary amines that play a critical role in the chemical-curing mechanisms of these types of materials. To combat this, some universal adhesive systems that don't use amine-free resin cements now include the use of a separately applied activator such as arylsulfinate salts. Adding another step creates more work for the clinician, so several universal adhesives (such as All-Bond Universal from BISCO) have been formulated with a lower acidity, so that they are compatible with most self- and dual-cure resin cements without the need for an activator.

ALL-BOND UNIVERSAL, A LIGHT-CURED UNIVERSAL ADHESIVE

"All-Bond Universal is less acidic, with a pH of 3.2, than other universal adhesives that have pHs that range between 2.0 and 3.0," Dr Alex explains. "This is enough of a difference to allow the reactions necessary for chemical curing of self- and dual-cure resin cements and composites when using All-Bond Universal."

Support Materials

Chemistry comes into play with the supporting cast of materials as well, including etchants, primers, and cleaners, all of which need to be chemically compatible with the composites, cements, and adhesives a clinician is using.

Etching is used to demineralize portions of the hydroxyapatite crystals in enamel and dentin to create a porous surface that allows tags to form in the dentin structure. Basically, the goal is to create pores that resin can permeate to attach to the tooth. This bond however is subject to enzymatic degradation from matrix metalloproteinases (MMPs) as well as hydrolytic degradation from pulpal fluid and moisture. MMPs are activated when the tooth's surface is demineralized due to etching with phosphoric acid and can degrade the collagen in the previously created hybrid layer. To combat this and deactivate MMPs, some manufacturers are including the benzoyl aluminum chloride molecule in etchants. Alternatively, clinicians can apply a separate 2% chlorhexidine solution after the phosphoric acid etchant is applied.

Etchants should have good thixotropic properties (Dr Alex looks for gels that aren't too thick or too thin, with good flow characteristics) and should be easy to visualize when placed. The consistency of the etchant also depends on which etching technique a clinician intends to employ. For selective etch, the etchant should be thicker, and heavier on the viscosity, so that the clinician can pinpoint the product specifically on the enamel surface. In a total-etch scenario, an etchant can have lower viscosity and be runnier so that it can cover more surface. Whatever the situation, you need to select the etchant that will be the most effective for that particular indication.

"You have to consider the color, the viscosity, and also the bonding technique, depending on what you want," Dr Nuñez says. "Sometimes it comes down to the nuances of a product, but it also depends on what is it that you're going to do with it."

Primers contain hydrophilic resin monomers combined with a solvent (usually water, alcohol, or acetone) that work to displace moisture to expand the collagen network and allow the monomer to infiltrate the collagen network. Primer molecules contain both

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hydrophilic and hydrophobic monomers, and penetrate the demineralized dentin matrix, increasing the wettability of the dentin surface, paving the way for the application of a hydrophobic resin.[7]

Many manufacturers are increasingly combining primers and adhesives into single-bottle formulations, but removing the additional priming step may not lead to increased clinical success. While this helps clinicians save time and reduce inventory, it may not be the most sensible option chemically.

"Some universal adhesives contain silane, but many studies show the most durable bond to silicate-based ceramics is still hydrofluoric etching, followed by the use of a dedicated and separately placed silane primer," Dr Alex says. "While single-bottle systems certainly make marketing sense, this may not be optimal with some materials."

Z-PRIME™ PLUS, A SINGLE-COMPONENT PRIMER FEATURING MDP

The use of primers may also necessitate the use of cleaners. For example, when bonding resin-based cement to zirconia, a zirconia primer is required, such as a 10-MDP. However, if the intaglio surface is contaminated during restoration try-in, the saliva will bind to the same reactive sites that the primer requires for chemical interaction.

"This competition for reaction sites significantly decreases the efficacy of zirconia primers, and it's necessary to 'free up' those sites so the zirconia primers can function optimally," Dr Alex says. "This can be accomplished by sandblasting the restoration after saliva contamination, or the use of a strongly alkaline cleaning solution."

Connecting Materials to Clinical Use

In summary, understanding the building blocks of materials can help clinicians choose the appropriate products to consistently build successful clinical outcomes.

"The ultimate criteria for any dental material is how it performs clinically—especially over time," Dr Alex says. "Dental materials are being produced at such a prolific rate that there is often inadequate time for clinical testing. While materials may perform well in in-vitro testing, this may not translate for clinical situations. In that sense, many dental materials are in fact being 'tested' on our patients."

This rapid rate of development makes knowing what is in materials—and how they interact—increasingly critical. In addition to the makeup of a material, it's also important to consider the clinical applications and prioritize which properties are crucial for each scenario.

"The critical properties of a material are dependent upon its clinical application," Dr Lawson says. "For example, the wear resistance of a resin cement is not nearly as critical as that of a resin composite. Materials also must be considered for how they are used in combination."

Dr Nuñez reemphasizes how this becomes particularly important when mixing products from different companies, as each manufacturer has its own formulation that may or may not be compatible with another brand.

"I think that it is very important for the clinician to understand the interaction of the products that they're using, whether they are from one company or whether they are from multiple companies," Dr Nuñez explains. "It is very important because that way, the clinician can make rational decisions on what to use, and he or she can be able to use those products properly."

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