The Dos and Don'ts of Bonding Zirconia

DENTAL PRODUCTS REPORT

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When some clinicians think of zirconia, they think of the zirconia of the past: strong but ugly, limited indications, and impossible to bond. However, with advances in esthetics and translucency, increased flexural strength, a growing list of clinical applications, and a much better understanding of the chemistry (and bonding options) of zirconia, it's time for clinicians to sit up and take notice.

By learning about and understanding zirconia's benefits and the steps needed to create a successful bond, clinicians can become more confident in providing their patients with better restorative options that meet their esthetic and structural needs. Plus, they will realize that bonding zirconia restorations isn't as hard as it seems.

"A misconception held by many dentists is that you cannot bond to zirconia," says Gary Alex, DDS. "The fact is you can bond very predictably and durably to zirconia surfaces using a combination of sandblasting, a phosphate ester primer such as 10-MDP, and an appropriate resin-based cement."

And the research supports this.

"It seems like there's a great divide between the majority opinion of the research community and that of the practicing clinicians," says Nathaniel Lawson, DMD, PhD, director of the Division of Biomaterials at the University of Alabama at Birmingham School of Dentistry. "In the published literature, there exist at least 4 systematic reviews of laboratory studies which conclude that a higher bond strength to zirconia can be achieved when the correct steps are performed to achieve mechanical roughening and chemical adhesion. Furthermore, a systematic review of clinical trials reports the clinical success of bonding to zirconia. But many dentists are unaware of the benefits."

So what are the benefits of bonding with zirconia, and what do clinicians need to know? It all starts at the molecular level.

The chemistry of zirconia

Most dentists know that zirconia is different from other materials, but they don't always understand why. The chemistry and makeup of zirconia make it unique, and also add to its numerous strengths. Understanding this chemistry can make a huge difference in realizing—and properly executing—these benefits.

"Zirconia is often referred to as 'white metal' or 'white steel,'" Alex says. "Of course, zirconia is not steel. In fact, it is not even a metal. Zirconia is a glass-free polycrystalline ceramic and is the oxide of the element zirconium. While the element zirconium is a tough, hard silvery white metal, its oxide, the zirconia we use in dentistry, is not."

As opposed to lithium disilicate, a glass ceramic, zirconia is a polycrystalline material. Lawson says the advantage of a polycrystalline material is that it is composed of many small crystals, which gives it strength.

"Glass ceramic materials also have some crystalline microstructure but it is held together by a glass matrix," he says. "This glass matrix is the weak link as far as crack propagation and it is the reason that zirconia is stronger than glass ceramic materials."

However, the lack of glass in zirconia changes the way in which the chemical bond is formed. Glass-based ceramics are chemically linked to resin cements linking a molecule called silane that bonds to glass on one side and resin on the other. In contrast, zirconia can be bonded with the 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) molecule, which then chemically links zirconia with resin.

And the chemistry of 10-MDP is fascinating. First synthesized in the 1980s by chemists in Japan, the molecule has 2 functional ends: The first, a methacrylate group, bonds to the methacrylate resins in resin cement. The second contains a phosphate-based functional group that can bond to zirconia through ionic or hydrogen bonding. Today the 10-MDP monomer is used in many adhesive systems and has many positive attributes for use in a bonding agent thanks to its composition.

"It is a versatile amphiphilic functional monomer with a hydrophobic methacrylate group on one end [capable of chemical bonding to methacrylate-based restoratives and cements] and a hydrophilic polar phosphate group on the other [capable of chemical bonding to tooth tissues, metals, and zirconia]," Alex explains. "On the tooth side, 10-MDP is one of the few monomers used in adhesive dentistry that has been shown to actually bond chemically to the tooth tissues. Likewise, MDP has been shown to chemically bond to zirconia."

And bond it does. Numerous laboratory tests have found the chemical bond between zirconia and 10-MDP to be impressive.

"The chemical bond between 10-MDP and zirconia has been proved by several different types of laboratory tests," Lawson explains. "One test is just to show that phosphorus atoms are present on the surface of zirconia after 10-MDP is applied and rinsed off. Another test is to show that the chemical bonds in the phosphate-based functional group of the 10-MDP change state when mixed with zirconia. A third test shows that when zirconia and 10-MDP are allowed to bond and their fragments are separated by atomic weight, fragments exist which correspond to pieces of bonded 10-MDP and zirconia. Finally, a test which looks at interatomic spacing reported interatomic distances between zirconia and the phosphate-based functional group that correspond to ionic or hydrogen bonding."

DO:
Understand the chemistry of the materials you choose for restorations and the corresponding chemistry required in the materials used to bond those restorations.

DON'T:
Confuse zirconium oxide—also known as zirconia, a ceramic material commonly used to fabricate dental restorations—with zirconium—a hard white metal that is element 40 in the periodic table.

Numerous indications, numerous benefits

Most dentists are familiar with the steps on bonding to glass-based ceramics—and may have a clinical track record of success when bonding—which can make them reticent to try a new concept. Lawson thinks dentists should take care to steer clear of this mentality and lose their skepticism about bonded zirconia.

"I believe the reason that many dentists are either unaware or mistrusting of the bond to zirconia is due to the fact that the bonding steps are completely different [from] those required for glass-based ceramics," he says. "However, bonded zirconia restorations offer some clinical advantages over bonded glass-based ceramic restorations, so it is advantageous for the clinician to understand how to bond zirconia."

And the advantages are numerous. One main benefit, according to Lawson, is zirconia's strength.

"Bonding zirconia can reinforce a restoration—ie, it can increase the force at which a restoration would fracture," he explains. "Zirconia bonding is indicated for increased retention or reinforcement of a restoration. Increased retention is needed for tooth preparations with short or over-tapered axial walls, as well as for nonretentive preparations such as overlays, veneers, or Maryland bridges."

Lawson also cites preparations with limited occlusal clearance as a good opportunity for zirconia. In these cases, a zirconia restoration can allow a reduced occlusal restorative dimension. If the preparation also lacks retention, the restoration may need to be bonded, and zirconia offers higher strength for connectors.

Advances in zirconia have only added to the list of benefits. Although traditional high-strength zirconia is ideal for masking discolored tooth preparations, its opacity has historically limited its use for other esthetic preparations. This led to the development of translucent zirconia, a desirable alternative for esthetic restorations. The 2 types have their own benefits.

"So-called 'high-strength' and 'translucent' zirconia differs in chemical makeup, crystalline configuration, physical properties, and optical qualities," Alex explains. "Typically, high-strength zirconia [approximately 3 mol% yttria concentration] has a higher flexural strength and fracture toughness than translucent zirconia [approximately 5 mol% yttria concentration]."

In its monolithic form, according to Alex, high-strength zirconia is particularly useful in the posterior regions, where maximum strength is necessary to resist higher occlusal forces. However, in anterior restorations, where esthetics are critical, the bright white color (and lack of fluorescence and transparency) of high-strength monolithic zirconia restorations can make them unappealing. This is where translucent zirconia becomes the better choice.

"Manufacturers employ a number of techniques to improve the translucency of zirconia including reducing grain size, reducing alumina content, [modifying] processing and pressing techniques, altering sintering times and temperatures, and manipulating dopant levels to increase the percentage of the more translucent cubic crystals relative to the more opaque tetragonal crystals," Alex says. "The trade-off is as the translucency increases, flexural strength and fracture toughness decrease."

This does mean that translucent zirconia is more vulnerable to cracking. However, despite this decrease in strength and the physical properties of translucent zirconia being less robust than those of traditional zirconia, they still significantly exceed of traditional PFM or lithium disilicate restorations, which makes them a good choice for many cases.

"Translucent zirconia is typically about midway between traditional high-strength zirconia and lithium disilicate in terms of both strength and translucency," Alex says.

DO:
Understand the clinical situations in which a bonded zirconia restoration will be the best option; for example, limitations on prep design or the need for high strength or high opacity.

DON'T:
Think zirconia has to be either very strong but also opaque and unesthetic, or translucent but weak.

Optimal tools and protocols for success

One of the biggest errors a clinician can make when bonding to zirconia is not having the correct tools to prepare, decontaminate, and bond the restoration adequately. The zirconia bonding process differs from that of other materials, so it comes as no surprise that the decontamination and cleaning processes differ as well—and are incredibly critical to the bond's success. This means that knowing the correct protocols—and having the right products on hand to implement them—is paramount to success.

Unlike other materials, zirconium oxide (the zirconia used in dentistry) bonds to phosphates. Because saliva contains a significant amount of phosphate, the phospholipids in saliva contamination can reduce the number of bonding sites, hindering the development of a strong bond. "Zirconia has a remarkable affinity for phosphate ions," Alex notes. "This affinity extends not only to the phosphate group in MDP but also to phosphate groups and ions that are inherent in saliva. When zirconia restorations are tried in and the intaglio surface is contaminated by saliva, the phosphate ions from the saliva bind to, and occupy, the same reactive sites that zirconia primers require for chemical interactions. This competition for reaction sites significantly decreases the efficacy of zirconia primers and it is necessary to 'free up' these sites so zirconia primers can function optimally."

Mechanical pretreatment

As it is impossible to shield the zirconia from saliva during try-in, it is critical to properly prepare and decontaminate the zirconia intaglio to remove the competition for bonding sites before final bonding. Other materials simply require chemical cleaning; for example, hydrofluoric acid and silane can be used for cleaning all-ceramic restorations, and glass ceramics can be etched with hydrofluoric acid to remove glass and create the surface roughness that allows it to mechanically interlock with cement. But zirconia takes some extra attention. Zirconia doesn't contain glass, so this etching strategy won't work. Instead, clinicians need to implement sandblasting or light particle abrasion to enhance bond strength by creating a fresh zirconia surface to bond to.

"It is not possible to achieve surface roughness by etching zirconia with the same hydrofluoric acid used to etch glass ceramics," Lawson explains. "Therefore, surface roughness is achieved through sandblasting with alumina particles. This step is critical in achieving a strong bond to zirconia."

As a rule of thumb, Lawson recommends using a pressure of 1 to 2 bar (15-30 psi). Although sandblasting is an important step, Alex emphasizes the need to avoid excessive pressure, which could cause damage to the zirconia surface.

"Particle size and type is also a consideration as, generally speaking, the larger [more massive] and harder the particle, the greater the force it imparts as it hits the target surface," he says. "Some studies have shown that traditional high-strength zirconia can be safely and effectively sandblasted with 30 to 50 μm aluminous oxide using a blast pressure of 1.5 to 2.0 bar [approximately 20-30 psi] from a distance of 2 to 3 cm."
Because translucent zirconia is not as strong as traditional zirconia, clinicians should be careful not to sandblast translucents with the same force. For translucent zirconia, Alex recommends that blasting pressures be in the lower end of the range, preferably at 20 psi, to avoid surface damage that could result in the reduction of physical properties.

DO:
Roughen the bonding surface of a zirconia restoration using a sandblaster.

DON'T:
Use an acid etchant on the surface of a zirconia restoration because it cannot achieve the desired roughness.

Chemical decontamination

A physical approach to decontamination isn't enough: You also need to attack saliva chemically. Findings from several studies show that a combination of chemical and mechanical pretreatment is necessary to ensure long-lasting, effective bonds.[1] As a result, after try-in, the saliva should be cleaned off with a strongly alkaline zirconia cleaner. These cleaners, such as ZirClean™ (BISCO), neutralize the ionic bond between saliva phosphates and zirconia. Potassium hydroxide (KOH), the active ingredient in ZirClean, reacts with the restoration surface and neutralizes phosphate contamination to expose new bonding sites.

Alex is quick to emphasize the importance of using an alkaline cleaner. "It should be pointed out that vigorous rinsing with water, or the use of acetone and alcohol, is not effective in cleaning zirconia surfaces that have been contaminated with saliva," he says.

In addition to the sandblasting and decontamination processes, zirconia primers are an excellent tool for increasing bond strength. Conventional silane coupling formulas cannot bind to metal-oxide ceramics, but ceramic primers have unique adhesive monomers that allow them to bond to zirconia. When bonding zirconia, the use of an MDP-containing primer is necessary as a silane primer won't create a chemical bond to zirconia.

"Using the correct materials to bond to zirconia is critical," Lawson points out. "A 10-MDP–containing primer should be applied to the intaglio surface of the restoration. After that, bonding to the tooth should follow the same steps as used when bonding any restoration, which includes the optional use of a tooth primer and required use of a resin cement."

And there are plenty of primer options on the market. For example, BISCO's Z-PRIME™ Plus excludes silane completely (as it doesn't increase zirconia adhesion) and is comprised exclusively of phosphate and carboxylic monomers.[2] In addition, there are primer-containing cements that negate the need for additional primer application, such as BISCO's TheraCem. These myriad options make it simple to adopt a primer that integrates seamlessly into a practice's workflow.

DO:
Make sure to clean all zirconia restorations with a strong alkaline cleaner to remove phosphates from the zirconia surface.

DON'T:
Forget to use a zirconia primer that contains MDP after cleaning the restoration and before applying the adhesive.

Cementation

Cements are another aspect to consider when bonding to zirconia. When using translucent zirconia, luting cements are generally a poor choice due to their opaque nature, which can overwhelm the translucency of the zirconia and disrupt shade matching. To preserve these esthetics without sacrificing bond strength, many clinicians are using resin cements for zirconia bonding. And they are proving to be effective: One study reported that zirconia crowns adhered with zinc-phosphate cement were twice as likely to fail than those bonded with self-adhesive dual-cure resin cement.[3]

However, not all zirconia restorations are the same. In preparations with insufficient retention, resin cements may be the best choice. But in many cases, the strength of zirconia suffices for a resin-modified glass ionomer (RMGI) cement to be implemented.

"If the preparations have adequate resistance and retention form, and esthetics are not an issue, then easier-to-use and clean ion-releasing RMGI cements, calcium silicates, or calcium aluminates are viable options," Alex says.

However, he notes, resin cements may be a better choice when dealing with translucent zirconia or zirconia restorations with minimal occlusal thickness. This is because resin-based cements allow better stress distribution when loaded, can inhibit crack formation, and optimize overall assembly strength.

"While dual-cure self-etching self-priming resin cements are popular with dentists because they do not require a separate bonding agent [to] be placed on the tooth, dentists should be aware that the highest bond to tooth structure is achieved by the use of resin cements used in conjunction with a separately placed bonding agent," Alex advises. "Resin-based cements used in conjunction with a bonding agent have a distinct advantage over RMGI and other conventional cements when it comes to bonding restorations on, or in, minimally retentive preparations, as they bond more durably and predictably to both tooth tissues and zirconia."

Whatever products you adopt, Alex reemphasizes that proper management of the zirconia substrate and tooth tissues is crucial for predictable and durable clinical outcomes. "As a general rule, the intaglio surface of all zirconia restorations [should] be sandblasted [using appropriate particle types, size, and pressures] and a zirconia primer placed [typically a phosphate ester such as 10-MDP]," he says. "However, this is not true in every situation, and the use of a separate zirconia primer is contraindicated or not necessary with some materials. In this regard, manufacturer instructions and recommendations should be followed precisely for optimal results."

DO:
Learn how the prep design affects the type of cement that will work best in a specific situation.

DON'T:
Forget to read and follow the manufacturer instructions for all materials used when bonding in zirconia restorations.

The bottom line

Advances in product chemistry and development and increased knowledge of zirconia are making zirconia bonding more predictable and effective than ever. Understanding the building blocks of zirconia can help clinicians prioritize the best products and protocols to ensure successful bonds, enabling them to create the long-lasting, durable esthetic restorations their patients deserve.

"It's advantageous for clinicians to understand how to bond with zirconia," Lawson says. "It offers clinical advantages over other materials, and the clinical success—as proved in clinical trials—is high."

References

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