Abstract

Fossil preparators have a range of adhesives to choose from and it is often difficult to select one most suitable for any given task. The adhesives that preparators use can be divided into two basic categories: solution adhesives, which include Paraloid B-72, Butvar B-76, Butvar B-98, and McGee B-15; and reaction adhesives, which include various brands of epoxies and cyanoacrylates. Both types of adhesives share some basic characteristics, however, solution and reaction adhesives differ fundamentally in the manner in which they set or solidify. Understanding the distinction between these two types of adhesives helps to explain differences in both their working and final properties. This information can assist the preparator in making an appropriate and successful adhesive selection when joining, consolidating or coating a specimen.
Introduction

Fossil preparators regularly use a range of adhesives in their work. Those most commonly utilized include Paraloid B-72 (an ethyl methacrylate co-polymer formerly called Acryloid), Butvar B-76 and B-98 (polyvinyl butyral), McGean B-15 (a polyvinyl acetate formerly called Vinac), and various brands of epoxies and cyanoacrylates.

With this collection of adhesives, preparators are required to perform a multitude of tasks including joining, consolidation, coating, and gap filling on a range of fossils which can differ greatly in size and state of preservation. Although these materials are used for considerably more than simply joining parts, collectively they can be referred to as “adhesives” because in all their applications it is their ability to adhere to themselves and other materials that makes them useful to the preparator.

Selecting the most appropriate adhesive for the task at hand is an important part of successful fossil preparation. No two fossils are exactly alike, and even the most experienced preparator is often faced with new challenges that require them to reevaluate an old approach or develop new solutions. Key to making a suitable selection is understanding that not all of these adhesive “tools” are interchangeable - some are more appropriate for particular tasks than others. There is no single adhesive that works best in every preparation situation.

The adhesives listed above can be divided into two basic groups according to how they set or dry: solution adhesives, which set by evaporation of a solvent; and reaction adhesives that set by chemical reaction. This paper will examine these two categories of adhesives as knowledge of the fundamental difference between these two types is an essential first step in making a successful adhesive selection.

What makes adhesives stick?

To understand what sets reaction and solution adhesives apart we must first examine how they hold things together. We know these adhesives stick things together - but how? The following is a brief answer to this question that relies heavily on several useful texts, including Horie (1987) and the three volume Science for Conservators series (Wilks, 1987 a-c).

All the adhesives commonly used by preparators are applied as flowing liquids that spread onto or “wet” the surfaces or substrates to be joined. Wetting is something we understand intuitively when we lick a finger to pick up a crumb or use wet sand to build a sand castle: a liquid on its own can act as an adhesive. This is due to an attraction called secondary bonding that exists between molecules, in this case between the molecules of the water and molecules of the sand or crumb.

Secondary bonding occurs when there is very close contact between molecules with positively or negatively charged sites or groups of atoms in their structure, causing the molecules to stick to each other like tiny magnets. These forces are significantly weaker than those involved in primary bonding, which is what holds atoms together to form molecules. Primary bonds are the very strong chemical bonds that hold the hydrogen and oxygen atoms together within a molecule of water (H₂O), while secondary bonds are the much weaker forces that exist between the molecules of water themselves (Figs. 1, 2). These forces are strong enough to hold water together so that it can form drops, but weak enough to allow it to spread onto surfaces.

FIGURE 1: Primary bonds are very strong chemical bonds that hold atoms together to form molecules.

FIGURE 2: Secondary bonds are relatively weak forces that occur when there is very close contact between molecules with positively or negatively charged sites or groups of atoms in their structure.
enough that the molecules of water can easily move apart and roll past one another so that water can flow.

Water can hold sand together but the resulting “castle” can easily be toppled or pushed apart; plain liquids can act as adhesives but they are generally not very strong ones. However, if the pile of wet sand is frozen, the adhesive strength of the water increases as the water solidifies, making it much more difficult to push it apart. This illustrates two important properties required of an adhesive: first, it must be liquid so it can properly wet or cover the surface; second, it must set or become rigid to prevent shifting or slippage when pressure or stress is applied from gravity or other outside forces.

Once the adhesive solidifies, the strength of the resulting bond depends on several factors. In the case of porous, rough, and irregular surfaces—such as those commonly encountered in fossil preparation—the strength of the bond is largely due to mechanical interlocking. The liquid adhesive flows into all the pores and crevices of the substrate, and once hardened, it mechanically locks the parts together. Surface contact and secondary bonding between the molecules of the adhesive and the molecules of the substrate continue to play a role, but the strength of the bond is greatly dependent on the cohesive strength of the adhesive, i.e. the strength of the bonds between the molecules of the adhesive itself.

Reaction and solution adhesives are both applied as liquids that become solid or “set” after application. Both bond to materials following the same set of rules described above: bonding relies on good wetting, surface contact, secondary bonding between the adhesive and the substrate, mechanical interlocking, and the cohesive strength of the interlocked adhesive. However, the structure and physical properties of these two types of adhesives differ fundamentally in both their liquid and solid forms, resulting in substantial differences in both their working and final properties.

**How are solution and reaction adhesives different?**

Solution and reaction adhesives are both polymers. Polymers are giant molecules formed by linking many small, simple molecules called monomers. Polymers make good adhesives because the many repeated units multiply the sites for attraction or secondary bonding. This structure enhances the ability of these macromolecules to entangle and attach to themselves or other materials. However, there is a fundamental difference between the structure of the polymers formed by solution and reaction adhesives.

Solution adhesives are linear or slightly branched polymers. This means that the monomer units of which they are formed are strung together in straight chains (Fig. 3), which sometimes have small side branches. They are applied as pre-made linear molecules that do not change their basic chemistry or structure as they set or dry. Reaction adhesives on the other hand, are applied as liquid monomers that chemically react to form solid polymers (polymerize) in place after application. The resulting structure is rigid, linked with primary bonds and often cross-linked into a network (Fig. 4). In other words, the solution adhesives remain a collection of individual molecules, while reaction adhesives basically form one large polymer molecule.

Solution adhesives such as Paraloid B-72, Butvar B-76 and B-98, and McGean B-15 are often purchased as solid polymeric materials (in the form of powders or beads) that can be mixed with organic
solvents such as acetone or ethanol to form liquids for application. Both the molecules of the liquid solvent and those of the solid polymers are held together with weak secondary bonds. If the attractive forces within the polymeric material are weaker than those between the solvent and the polymer, the polymer molecules will be pulled apart and go into solution. The linear polymer molecules are still intact but are separated and floating in the solvent like strands of pasta in water.

As the solvent evaporates the polymer strands come into closer contact, re-establishing secondary bonds with each other and also becoming physically entangled, forming a solid mass (Fig. 5). If solvents are reapplied at a later date the chains can still untangle and separate again forming a liquid. Some solution adhesives can be redissolved in this way repeatedly and indefinitely, because the polymeric material remains chemically unchanged before and after “setting”.

Reaction adhesives such as epoxies (Devcon, Epo-Tek, etc) and cyanoacrylates (Aron Alpha, Paleo-bond, etc) are purchased as liquid monomers which chemically react after application to form very large, rigid, polymers (Fig. 6). However, epoxies and cyanoacrylates form these structures in different ways. Epoxies are sold as two separate liquids: a resin and a hardener, which chemically react to form a cross-linked network when they are mixed together. Cyanoacrylates are sold as a single liquid which is a monomer, usually combined with an acid which prevents formation of the polymer before application. When the monomer comes in contact with the trace moisture naturally present on the surfaces to which it is applied, the acid is neutralized and polymerization occurs. The structure of cyanoacrylates is variable and may or may not be cross-linked, but it is generally strongly interconnected like the networked structure of epoxies (Repensek, 2003; Petrie, 2007).

Both types of reaction adhesives undergo chemical change in the solidification or setting process, and unlike solution adhesives, strong primary bonds are formed. Once set, the resulting material can not easily be dissolved or broken down. Some organic solvents may swell or soften the structure making it easier to break it apart physically, but commonly used organic solvents, such as acetone and ethanol, will be unable to separate the strong primary bonds holding these polymers together.

How differences between solution and reaction adhesives affect their final properties

Resolubility—The organic solvents commonly used by fossil preparators can easily redissolve solution adhesives as they are held together with weak secondary bonds, but are not effective on reaction adhesives which are held together by strong primary bonds. There are some instances when reaction adhesives can be softened with solvents and removed successfully, such as when they are used on a very small scale. However, in almost all cases removing or reducing reaction adhesives will require more time, effort, and far greater risk to the fossil.

Resolubility can be advantageous as field work often requires temporary application of consolidants or coatings, and lab work often involves multiple stages of applying, adjusting, removing, and reapplying adhesives to protect surfaces or support parts as matrix is removed. Resolubility is important in long-term as well as short-term or temporary applications. It is always preferable to use something reversible or reworkable if possible. Fossils are very commonly repaired, disassembled, stripped of coatings, and re-prepared for molding, display or for research; the future uses and requirements of the fossil are not always foreseeable and resolubility is therefore almost always an advantage.

There are some rare cases where resolubility may be undesirable, such as smaller, more delicate joins that could dissolve by accident if the surface was exposed to a solvent during cleaning or application of a coating in preparation for molding. More commonly, there can be instances where reversibility is sacrificed because reaction adhesives offer properties not available with solution adhesives, such as the ability to penetrate into hairline cracks or great strength.

Strength—Generally, the primary bonded reaction adhesives are harder and more rigid than the secondary bonded solution adhesives: they have greater cohesive strength. This is why epoxies are often used when the joined parts are so large or heavy that more resoluble solution adhesives might fail due to the stresses of gravity over time. The hardness and
rigidity of reaction adhesives also makes them useful when specimens must withstand extreme stresses during preparation, such as the impact of a chisel or powerful air scribe.

It should be noted that it may be possible to exploit the strength of epoxies without sacrificing reversibility. Barrier layers of solution adhesives such as Paraloid B-72 can be applied prior to application of an epoxy in order to allow for greater reversibility of the join in the future. It has been shown that this technique, if executed properly, can be used without negatively impacting the strength of the join (Podany et al., 2001). Soluble barrier layers can also be used to increase reversibility when reaction adhesives, such as epoxy putties, are used to fill gaps.

It is also important to note that stronger is not always better. The relative “weakness” of solution adhesives can be advantageous in some cases. In addition to being resolvable, these adhesives require less force to remove mechanically without the aid of solvents. Thus solution adhesives often work better than reaction adhesives when preparation requires temporary consolidation of loose matrix or application of temporary coatings which will later be removed with needles or air scribes.

In addition, very hard and rigid adhesives like epoxies and cyanoacrylates generally lack elasticity or flexibility unless they are heavily modified with additives. The ability to give or stretch under strain can be an important quality in a successful adhesive, as it allows it to move and bounce back under certain forms of stress rather than breaking or transferring the stress to the object and potentially causing damage. Generally it is undesirable for an adhesive to be more rigid or harder than the substrate as this can lead to damage in the original material. If the adhesive used in a join has more cohesive strength than the fossil itself, applied stress may fracture the fossil rather than the adhesive, resulting in characteristic fresh breaks parallel to the original join. Similarly, consolidation of soft substrates with very hard adhesives can cause zones of weakness due to incomplete and uneven penetration. Flexibility is a particularly important consideration when selecting an adhesive for use on sub-fossil or other materials that may expand and contract in reaction to fluctuating environmental conditions, such as relative humidity.

One of the reasons Paraloid B-72 is often favored by conservators is that it exhibits a moderate hardness and a specific balance between flexibility and rigidity that renders it a successful general purpose adhesive for a variety of materials (Koob, 1986). It should be noted that not all solution adhesives possess this balance and some, like certain grades of polyvinyl acetate, can be soft and rubbery enough at room temperature to be problematic. If used in joins they can slowly creep or move over time and eventually fail, and as surface coatings they can be sticky and trap dust and grime (Horie, 1987: 92). These adhesives become even softer at elevated temperatures, which could be problematic in hot field or storage environments.

Aging—When adhesives are used for long-term applications it is preferable that their aging properties are well understood and proven to be good. Poor aging of an adhesive can lead to a variety of undesirable results including shrinkage, distortion, embrittlement, decreased solubility, and darkening or yellowing over time. Damage from poor aging of adhesives can be found in most fossil collections, often

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**FIGURE 5:** Solution adhesives remain a collection of individual molecules held together by secondary bonds and entanglement.

**FIGURE 6:** Reaction adhesives basically form one large molecule held together by primary bonds.
including joint failures, and embrittled, lifting coatings that have damaged the surface of the bone.

When solution adhesives are purchased as powders or beads they are generally single ingredient products, containing only the pure polymeric material. This makes it easier to assess and predict their aging characteristics, and many solution adhesives are known to have excellent aging properties, especially Paraloid B-72 (Down et al., 1996; Feller and Curran, 1975; Lazzari and Chiantore, 2000; Chiantore and Lazzari, 2001). Polyvinyl acetates are reportedly somewhat less stable than Paraloid B-72 but are still generally considered to have very good aging properties (Feller and Curran, 1975; Horie, 1987: 92). The long-term aging of polyvinyl butyrals has been questioned in the past but recent studies indicate it is also a very stable material (Feller et al., 2001).

In contrast to the solution adhesives, reaction adhesives are often fairly complex formulations, with ingredients that can vary from one manufacturer to another. Formulas can change according to availability and cost of ingredients, and they often include additives that can affect aging. Even in formulations with fewer additives, it is difficult to know exactly what you are using: the terms “epoxy” and “cyanoacrylate” both denote a large and varied category of resins. The materials within these categories share some basic chemistry, but may differ significantly in their properties, which can make it more difficult to make general statements about many aspects of their behavior including aging.

The aging of epoxies has been studied in connection to the conservation of glass and many formulations have been found to yellow severely (Down, 2001b). Yellowing is generally considered a sign of degradation and may be indicative of other changes in the material over time. The epoxies that have been shown to yellow the least are those with few additives that have been formulated for use in art conservation or for optical applications, such as Hxtal NYL-1 and Epo-Tek 301-2 (Down, 1986). While these epoxies have very long set times that make them impractical for many preparation tasks, others with more reasonable setting times have also been shown to be relatively stable and have found use in the conservation of stone, including Araldite AY103/HY991 (Down, 1984, 1986 and 2001b; Podany et al., 2001).

All epoxies are subject to user error: imprecise measurement of the components and inadequate mixing can interfere with the chemical reaction, resulting in incomplete polymerization and poor aging. This is especially true of very fast-set epoxies such as 5-minute formulas that can harden before the components have a chance to fully react. These fast-set formulas may contain additives that make them quick, easy, and convenient for casual consumer use, but make them poor choices when the goal is producing the best possible bond with the most predictable behavior over time (Horie, 1987: 173). In addition, all epoxies have a very limited shelf-life, of about one year. Epoxies that are past their shelf-life may appear to set after mixing but may not have polymerized properly and might eventually deteriorate, so it is always preferable to discard old epoxies and to use freshly received material (Down, 2001b).

Cyanoacrylates have found increasingly wide use in fossil preparation since the late 1970’s (Howie, 1984; Rixon, 1976). However, the aging behavior of cyanoacrylates has not been fully investigated. This is partially attributable to the fact that they have not been used widely in the field of art conservation, which has initiated many of the previous assessments of adhesive stability applicable to fossil preparation. One published study of cyanoacrylates has shown that there are still many unanswered questions regarding their stability and that contact with some fossils may accelerate degradation of cyanoacrylates (Down and Kaminska, 2000). The unique properties of cyanoacrylates, such as their superior ability to penetrate into hairline cracks and fast set time, may override questions about their aging in some instances, but care should be taken to avoid using them when more fully investigated adhesives could do the same job.

It should also be noted that not all solution adhesives have good aging properties. Cellulose nitrate, often found in household glues such as Duco Cement, becomes very brittle, shrinks, yellows, and weakens with age, often leading to bond failure (Horie, 1987: 133-134; Koob, 1982). Other solution adhesives can become harder and less soluble with time by cross-linking (forming primary bonds), like cross-linking reaction adhesives. This is true of some natural resins such as shellac and also some modern synthetic resins such as Paraloid B-67, which is sometimes used as a resistant coating for acid.

Emulsions or “white glues” (such as Elmer’s Glue-All) are a special class of water-born solution adhesives, many of which are known to deteriorate with age (Horie, 1987: 94-96,110-112). These adhesives consist of minute particles of non-water soluble polymers such as polyvinyl acetates or acrylics which are suspended in an aqueous solution. They set by evaporation of water, but are water soluble only before they are fully set. Once set, the resulting polymer film is only soluble in non-aqueous solvents such as acetone, toluene, and xylene. These adhesives are complex formulations as their suspended state is achieved and maintained through the addition of various materials such as emulsifiers, stabilizers and dispersing agents, and the compositions often include many other additives including plasticizers, thickening agents, and biocides. The quality of these adhesives varies greatly and the formulations commonly sold for home use (Elmer’s, etc) can become hard, brittle, discolored, and insoluble over time (Down et al, 1996; Johnson, 1994:226). Other specialty formulations of emulsions or dispersions, particularly the acrylics, may fare better over time, including certain grades of adhesives with the trade names Acrystal, Primal, Rhoplex, Jade and others (Down et al, 1996; Johnson, 1994). However, even these “better quality” white glues are only recommended for use when a water based adhesive is required, such as in the consolidation of wet specimens in the field.

How differences between solution and reaction adhesives affect their working properties

Working and Setting Times—The working time and set time of solution adhesives are dependent on the volatility of the solvent used. The solution adhesives mentioned in this paper can be dissolved in a range of different organic solvents with diverse rates of evaporation. This property can be exploited to vary the working and setting time of an adhesive to meet the requirements of a specific task. Conveniently, acetone and ethanol, the two solvents most commonly found in the prep lab and field, present a range of volatility from fast (acetone) to moderate (ethanol), and almost all the solution adhesives listed in this paper are soluble in both of these solvents. Thus the working and setting times of a single resin, such as Paraloid B-72, can be adjusted by dissolving it in different solvents: mix it in acetone for quick setting, or with ethanol for slower evaporation and longer working time. Temperature and air-flow can also affect working times of adhesives that set by evaporation; evaporation can be slowed by covering the specimen to reduce air-flow, and these adhesives will set more quickly if used out in the hot sun in the field. Working time of solution adhesives can also be affected by volume; application of tiny drops for micropreparation can be difficult because they harden too quickly due to a high surface-to-volume ratio which speeds evaporation.

Most cyanoacrylates set relatively quickly and are thus sometimes preferred when clamping is not possible, although often a solution adhesive in acetone can set as fast. Because polymerization is initiated by surface moisture, cyanoacrylates do not usually harden until they make contact with the substrate, thus they can be applied as tiny drops. They also set more slowly in dry conditions and more rapidly in humid conditions, which is why some preparators speed setting with their breath. The use of cyanoacrylate accelerators such as sprays for an instant bond is not recommended because of their commonly observed tendency to turn fossils bright green, yellow or blue, reportedly in reaction to iron (Howie, 1984).

Epoxies naturally set slowly and the long working time of epoxy allows plenty of time to align and adjust fragments before setting. This can be useful for small, complex joints such as multiple broken cusps on small teeth. Epoxies can be used for consolidation of fine cracks; although viscous they can penetrate well because they have slow set times which allow them more time to flow. This is especially true of very slow setting epoxies (Epo-Tek 301-2, Hxtal NYL-1) which can take days to set. Epoxies with very fast set times, such as 5 minute formulas, have added accelerators and these additives can lead to an inferior product.

Viscosity—Viscosity is defined as the resistance of a liquid to flow. The more viscous the adhesive, the thicker it will be and the slower it will be to pour and spread. The viscosities of solution adhesives can be modified easily by adjusting the concentration of the polymer in the given solvent. Paraloid B-72 can be mixed in concentrations as low as 1-5% to produce a dilute low viscosity resin for consolidation, or in concentrations as high as 35-50% to produce a thick adhesive for joins. A high viscosity mixture of
Paraloid B-72 in acetone loaded into a tube, commonly used by conservators, is very useful and convenient for quick assembly of fragments, and can often be used in place of commercially packaged fast setting epoxies and cyanoacrylates, which while convenient, are not as resoluble and do not have as good aging properties as Paraloid B-72 (Koob, 1986).

One problem with solution adhesives is that their viscosity is directly linked to their concentration or polymer content. The only way to produce a low viscosity adhesive is to have a dilute or low concentration solution; one may get the adhesive solution into place but once the solvent evaporates relatively little actual adhesive polymer remains. This is not true of the reaction adhesives because they do not contain solvent. Therefore, it is possible to have low viscosity epoxies and cyanoacrylates with 100% monomer content, all of which reacts to form the polymer. This can be advantageous for very small joins and hairline cracks, where the need is to get a significant amount of adhesive into a very small space.

Penetration and Migration—The volatile solvent component of solution adhesives causes the polymer to migrate during solidification. The solvent is the carrier for the polymer: it carries it in, but also carries it back out as it evaporates and the polymer can often end up deposited on or close to the surface. The propensity of solution adhesives to migrate to the surface with the solvent can be problematic when one is trying to achieve deep consolidation. Migration of solution adhesives can be moderated by a variety of factors that have been discussed in the conservation literature, including solvent selection and control of drying conditions (Domaslowski, 1987-88; Hansen et al, 1993).

Reaction adhesives have no volatile solvent component and thus do not have a tendency to migrate out after penetration. They are applied as liquids composed of monomers, which are much smaller, more compact molecules than the linear or branched chain polymers of the solution adhesives. Thus they are more able to travel into the open spaces in the substrate, potentially achieving deeper penetration. This is especially true of cyanoacrylates which are not only composed of small monomer molecules but can also have very low viscosities without being dilute. However, low viscosity cyanoacrylates are also known to have poor gap filling properties (Down, 2001a: 36). Thus they may achieve deep penetration without successful consolidation in instances where there are large cracks or voids that need to be filled in order to stabilize the specimen effectively.

Reaction adhesives migrate less and have the potential to penetrate better than solution adhesives, but their insolubility, hardness, and questionable aging characteristics may outweigh these advantages. It should also be mentioned that in some cases deep penetration of the adhesive may not be necessary to achieve adequate consolidation, as superficial consolidation with more stable solution adhesives is often very effective at binding together difficult material in the field and the lab, and for many specimens this may be adequate or even preferable to using reaction adhesives.

Conclusion

The solution and reaction adhesives commonly used in fossil preparation are all polymers that are applied as flowing liquids, which solidify in place and become interlocked with the porous and irregular surfaces of fossils. However, they change from liquid to solid in fundamentally different ways resulting in significantly different products.

Many solution adhesives, including Paraloid B-72, McGean B-15, and the Butvar resins, solidify by evaporation of solvent and form masses of polymer chains held together by entanglement and secondary bonding. These adhesives can be custom mixed in different solvents and offer a versatile range of setting and working times, as well as viscosities. Because they set by solvent evaporation, they tend to migrate to the surface, which can be problematic for some applications, but this behavior can often be countered with various application and drying methods. The resulting adhesives are known to have very good aging properties, remain resoluble over time, and possess a range of cohesive strengths, which, although generally lower than those of reaction adhesives, are appropriate and sufficient for most preparation tasks.

Epoxies and cyanoacrylates set by chemical reaction to form large, primary-bonded polymers. They are not as versatile as solution adhesives: to obtain variations in setting time and viscosity they must be purchased in different commercial formulas, often containing additives that make it difficult to evaluate and predict their stability. Because they do not set by evaporation, they do not migrate toward the surface during setting, and it is possible to have
low viscosities without dilution. These traits, as well as their great cohesive strength, make them very useful in some instances. However their questionable aging properties and the insolubility of their strongly-bonded structures means they should only be used when the more versatile and stable solution adhesives cannot be used successfully.

There is no universal adhesive that will fulfill every application, and it is usually necessary to compromise when selecting a practical adhesive system. The selection process is difficult because many factors only briefly mentioned here must be considered, including the need for a full initial assessment of the specimen and its required treatment, and an understanding of the more subtle differences between the different individual adhesives and how to manipulate them with different mixing and application techniques. However, understanding the basic differences between the solution and reaction adhesives should equip the preparator with some of the fundamental information necessary to make the most appropriate and successful choice.

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