SEARCHING FOR THE FILLER OF MY DREAMS– AN ODYSSEY IN GAPS AND GLUES

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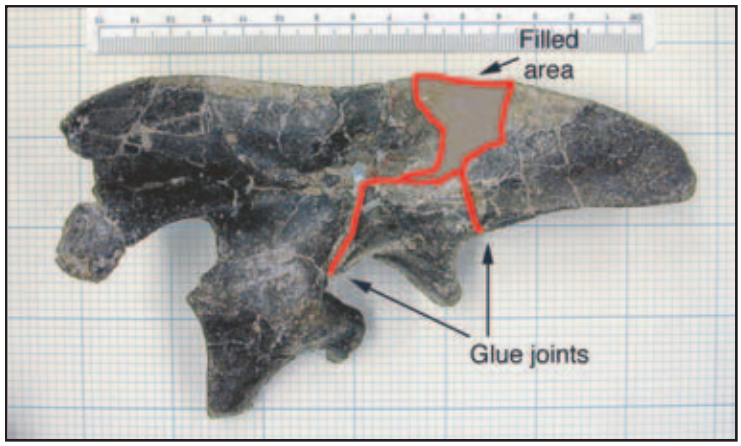
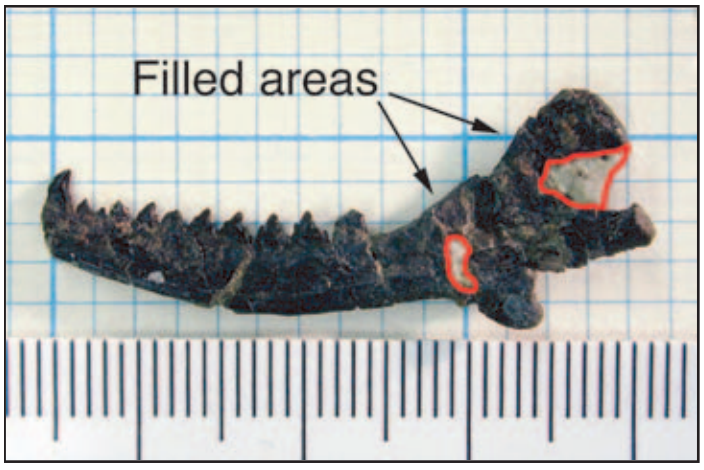


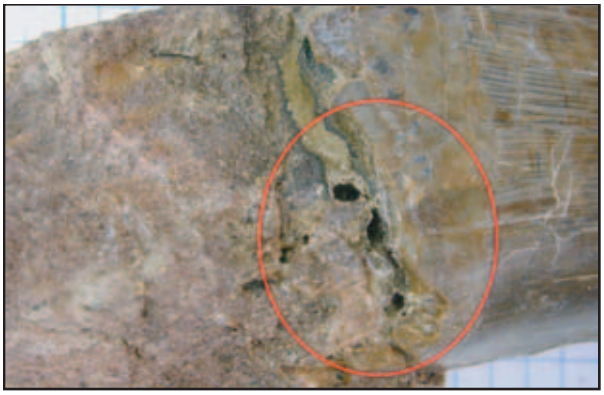
I'm sure that we're all familiar with this type of situation, where two pieces of broken bone are joined at only a relatively small area. Of course, these areas must have support or they will only break again. It is often necessary to bridge a gap for display purposes or to reconstruct an area to form a strong support for a cantilevered area of bone. I have been using various products as fillers for these kinds of areas, and as time has gone on, for one reason or another I have found them lacking.

So, I have begun some personal research to try to find other products, or mixtures of adhesives and fillers that might answer better for this kind of situation. With larger bones I do not feel that this is such a problem, either plaster or epoxy putty can be used and can even be removed without much danger to the specimen. But on very small specimens, I really feel that it is important to have control over the materials used for gap filling. Qualities desired in fill materials change with scale changes - microscopic fills are quite different from larger fills. Many materials, such as plaster, that may be acceptable or even preferable for larger bones may be undesirable at a small scale. In this paper I'll continue to focus on a gap filler for really small things. And I want to stress here that I will not be recommending or negating any product, I am only seeking a filler that meets this particular need. There are too many products and too many differing situations for me to feel comfortable with only one answer for all problems.

One of the materials that is often used is epoxy putty of one sort or another. That's what I used on this specimen. I think that it is fine for most cases. It has a great putty-like feel, is strong, is very easy to work with, and leaves a nice finished surface. However, it is difficult to remove, even with a barrier layer of Paraloid B72. It may require grinding which can put the original break in danger of breaking again.

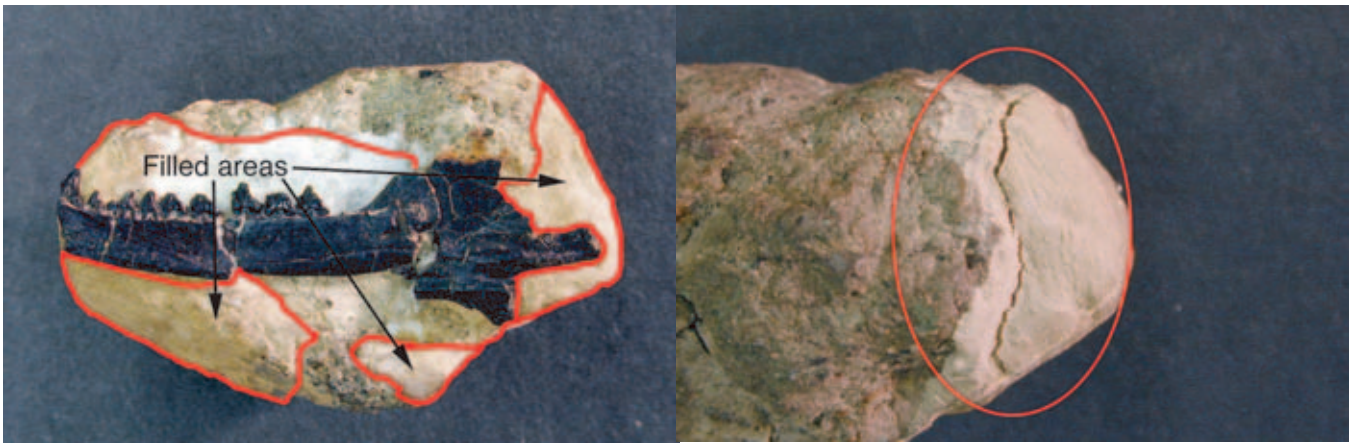


Perhaps, if I never changed my mind, or if that particular bit of bone that has been missing for 100 years never reappeared that would be fine, but it does happen.



So, I've primarily been using Paraloid B72 filled with Cab-O-Sil or microspheres. This is somewhat difficult to work with. Using acetone or alcohol to clean the surface, one runs the danger of dissolving the original adhesive joint as well. Additionally, Paraloid B72 being somewhat viscous can be expanded by the acetone evaporating from within it. You see the problem here. Vacuities can be left within the break. This both weakens the joint and is unsightly.

Someone recommended using DAP, a kind of vinyl spackle, sometimes used by ceramics conservators. It looks fine here on this side of the specimen but DAP shrinks on drying, is quite soft and must be consolidated after it dries. And it worried me, if it's shrinking this much on the outside, can it really be giving any support? Am I only consolidating the outside of the filled area or is there enough penetration to harden the DAP fill? This jaw was being set up for molding, so a more long-lasting support wasn't needed, but I wouldn't feel comfortable with this long term.



Then, the desired qualities in a gap filler are:

1. It should be strong enough to support the fossil, but not very much stronger than the bone.
2. It must be relatively non-flexible, and it shouldn't shrink, crack, soften or become brittle over time.
3. It should be readily removable, preferably by dissolving, or manually if that doesn't require too much force.
4. It should not be made of a material that cross-links over time and becomes insoluble.

The only solvents that I feel comfortable with in my lab for regular use are water, acetone, and ethanol. And if possible, I would prefer water as a dissolving agent, because I plan to continue using Paraloid B72 dissolved in acetone as an adhesive. With either acetone or ethanol as an adhesive solvent there is a risk of redissolving the original bond.

The ideal filler should be workable – so that the surface can be sculpted easily. Texture and color present other problems in a filler. Some of these are purely esthetic objections, as in a filler that has a grain size that is too large for the scale of the specimen. If the fill is just below the surface of the bone, is smoothly sculpted, and is a neutral color, it shows the viewer just where the bone begins and ends, and covers the least amount of information.

Researching the conservation literature and looking through supply catalogs, I came up with a number of likely looking candidates for adhesives as binders, fill materials, and a few pre-made fill products. I then tried to come up with a standardized system for testing each material, sculpting it and cleaning it, as if it were on a specimen.

METHODS

I used either a purchased adhesive product at 100% or made stock solutions of bead/granule adhesives dissolved in a solvent to 25-50% by weight, depending on the adhesive. I attempted to mix the various products in a standard way. However, because the characteristics of each product differed, I, somewhat arbitrarily varied the mixture as needed to make each as close as possible to the thickness or thinness of a binder as I would actually use it. The adhesive needs to be fairly high in solids to work well as a binder with a fill.

To 2ml of adhesive stock solution, filler was added by 1/4 teaspoonfuls until reaching a paste-like consistency. This varied with adhesive and with filler. All mixing of fills was done under a fume hood.

I used the purchased products according to directions.

I sought some shape that would resemble the types of fills that I have encountered without having to actually use, and risk damaging, a specimen. The adhesive/filler mixtures were applied to a screen with approximately 1/10th inch squares.

I did two samples for each mixture. One blob was left untouched until dry, the other sample I worked on, cleaning and sculpting as if it were on a specimen. 142 samples were made. Adhesives were grouped in Sets, and Tests were repeated using each of the fill materials. For example, Set/Test 1/6 was a mixture of Paraloid (Acryloid) B72 @ 50 % in acetone with Kaolin. Comments were noted for each sample on appearance, workability, surface smoothness, removal agent, and sculptability after drying.

With the best materials from the first test, I did a second test of sculpting the material into a 90∞angle formed by two pieces of 1/16th inch basswood glued at the corner with Paraloid B72. Five materials were chosen for the second test.

Adhesives sampled, from left back: Gaylord pH Neutral, Primal (Acrysol) WS24, Butvar B98, Golden Modeling Paste, Jade R, Evacon R, Rhoplex B60A, AYAF; from left front: DAP, Lineco Neutral, Promacto A 1023, Butvar B76, Vinac B25, Aquazol 200, Paraloid (Acryloid) B72.

ADHESIVES

Adhesive/Product	Description	Concentration
Paraloid (Acryloid) B72	ethyl methacrylate co-polymer	50% in acetone 25% in 50/50 ethanol/acetone
Butvar B76	polyvinyl butyral	25% in acetone
Butvar B98	polyvinyl butyral	25% in ethanol
Aquazol 200	poly(2-etyl-2-oxazoline)	50% in water
Evacon R	ethylene-vinylacetate co-polymer emulsion	100%
Primal (Acrysol) WS24	acrylic colloidal dispersion	100%
Golden Modeling Paste	acrylic polymer emulsion	100%
DAP Vinyl Spackle	PVA emulsion, calcium carbonate	100%
Rhoplex B60A	acrylic polymer emulsion	100%
Jade R	polyvinyl acetate	100%
Promacto A1023	polyvinyl acetate	100%
Gaylord pH Neutral White Adhesive	polyvinyl acetate	100%
Lineco Neutral pH adhesive	polyvinyl acetate	100%
Vinac B25	polyvinyl acetate	50% in acetone
AYAF	polyvinyl acetate	50% in acetone

NOTE: in most of the literature polyvinyl acetate and polyvinyl alcohols are referred to by name or just as PVA, not by brand name, manufacturer, or supplier.

Just a couple of notes on these:

- Jade R is a reversible form of Jade 403
- Aquazol 200 is also soluble in ethanol, acetone and water. The 200 refers to the molecular weight, it is also available in 50 and 500.
- Vinac B25 has a higher molecular weight than B15.
- Golden Modeling Paste seemed too thin by itself to use solely as a filler, so I used it as an adhesive.
- DAP Vinyl Spackle is listed here as an adhesive, I thought that perhaps by adding a filler to it I might control some of the shrinkage.
- Rhoplex B60A is a replacement for Rhoplex AC33, which I found often mentioned in conservation literature.
- Evacon R, a product unknown to me, is similar to Elvace, a product often mentioned in conservation literature.

Because most of these products were mentioned positively in some respect in conservation literature although not always as binders for fills, I felt reasonably comfortable with them. Also I deal here with only their working qualities for this very limited purpose. I have reservations about some, particularly the polyvinyl acetate emulsions that tend to cross-link over time.

FILLERS

Product	**Description**
Cab-O Sil	fumed silica
Hi-Sil #233	fumed silica
Microspheres	glass microballoons, sodium borosilicate
Microfibers	West System #403, proprietary blend containing cotton flock
Marble dust	calcium carbonate
Kaolin	aluminum silicate clay

□ West System #403 Microfibers is essentially a cellulose fiberfill.

□ Kaolin is a fine-grained clay powder. Pure kaolin is white, this product is much, much cheaper and still very fine-grained, but has some impurities, giving it a yellowish color.

□ Hi-Sil #233 is much the same as Cab-O-Sil. In fact, it proved so similar that some tests using it as a fill were not repeated

READY-MADE PRODUCTS

Product	**Description**
Magic-Sculpt	Epoxy putty with
□ □ □	alumino-silicate fillers,
□ □ □	titanium dioxide
Milliput	Epoxy putty with
□ □ □	alumino-silicate fillers,
□ □ □	titanium dioxide
LePages Polyfilla	Cellulose, gypsum
□ □ □	(calcium sulphate)
Plaster of Paris	Calcium sulphate
Hydrocal Plaster□	Calcium sulphate

LePages Polyfilla, a cellulose filler is essentially a mixture of plaster and cellulose.

Given all these substances, there are at least three factors of variability.

1. Adhesive. Even adhesives of the same type are very variable, depending only partially on chemistry. Some products have more solids, varying the viscosity.
2. Fill material. In addition to differences in the materials themselves, more or less material can be added, changing viscosity, workability and finished strength.
3. Reversal Agent. Water, alcohol, acetone or manual removal.

So, what were some results?

Beginning with the ready-made products….

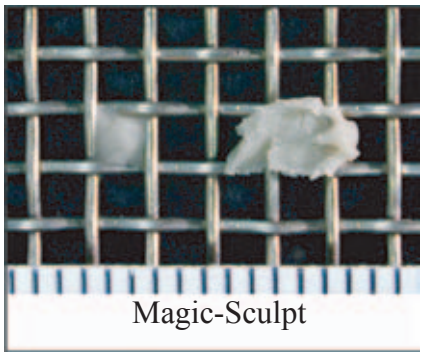
Magic-Sculpt is the epoxy putty that I usually use, particularly for large material that needs extra support. But, like all epoxy putties, it is permanent so it must be removed manually and in some cases this can be damaging to the specimen. It can be smoothed with water. The finished surface is very slightly rubbery.

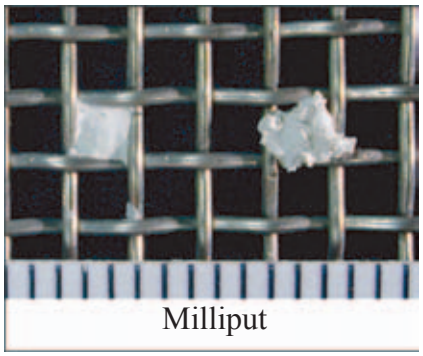
Milliput has a finer surface than the Magic-Sculp, but still must be removed manually. It has a less rubbery surface than Magic-Sculp.

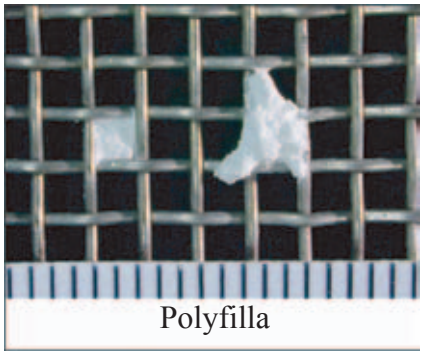
The Polyfilla shrank somewhat, though less than the DAP and had little adhesion. There might be instances where adhesion of the fill is not desired.

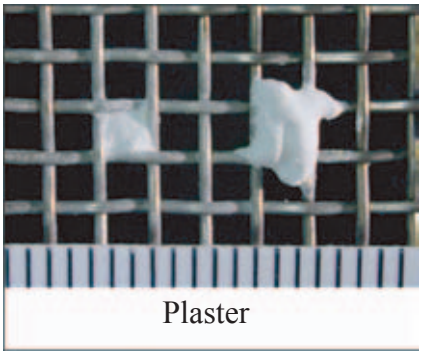
The Plaster of Paris was soft, and had no adhesion. It also leaves a white film outside of the sculpted area, when sculpted while damp. Plaster becomes softer and brittle with age.

Hydrocal Plaster has some of the same qualifications as Plaster of Paris, but is harder.


Magic-Sculpt

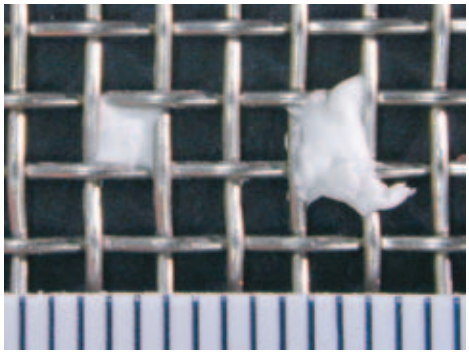

Milliput


Polyfilla

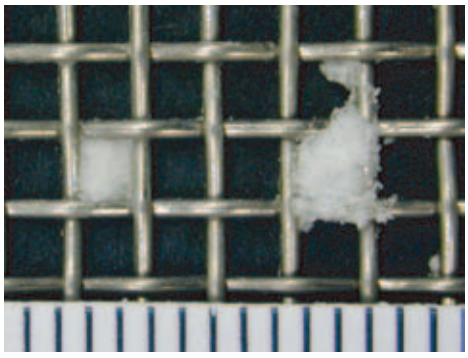

Plaster

And proceeding to the fill materials.

Of these, the marble dust was by far the nicest, giving a firm, smooth finish with almost all of the adhesives and remaining sculptable after drying. It left a slight whitish film, which could be brushed away.



Set/Test 11/85 Aquazol 200
50% in water with marble dust

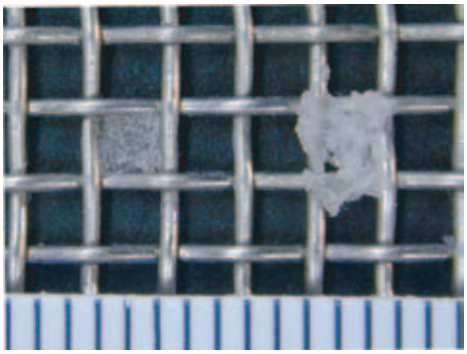


Set/Test 2/10 Paraloid (Acryloid) B72 25% in
50/50 ethanol/acetone with microbeads

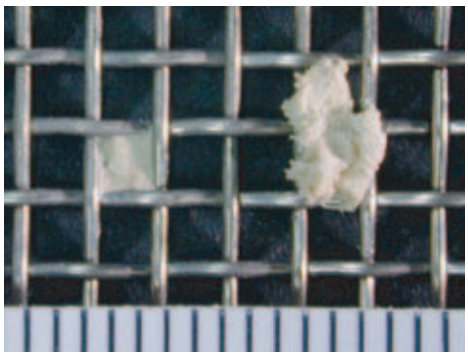
The microspheres were quite noticeable under the microscope. In addition for some reason as yet undetermined the addition of microspheres to some adhesives caused severe clumping, rendering those mixtures unusable. The affected products included: Jade R, Promacto A 1023, Gaylord pH-Neutral White Adhesive Lineco Neutral pH Adhesive and Evacon R.

While Kaolin and Cab O Sil work well and were smoothable, they still had a slightly lumpy appearance. The yellowish Kaolin that I chose seemed to whiten with some adhesives.

Cab O Sil additionally requires the addition of a pigment, as it is quite translucent. Of course, all of the fills would probably be tinted, but that it yet another variable and isn't dealt with here. Hi-Sil proved to be the same as Cab O Sil, so some tests were not repeated with that product.

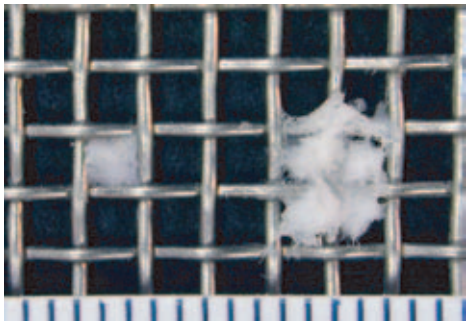


Set/Test 5/33 AYAF polyvinyl acetate
50% in acetone wit Cab O Sil



Set/Test 3/22 Butvar B76
25% in acetone with Kaolin

Microfibers remain puffy, with all adhesives, and cannot really be sculpted. They could perhaps be of use in pre-filling larger gaps.

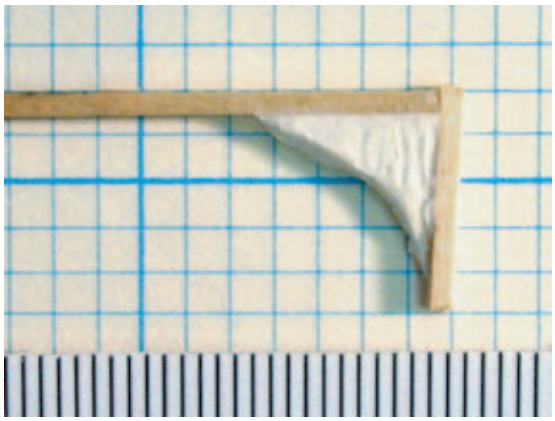


Set/Test 1/4 Paraloid (Acryloid) B72
50 % in acetone with microfibers

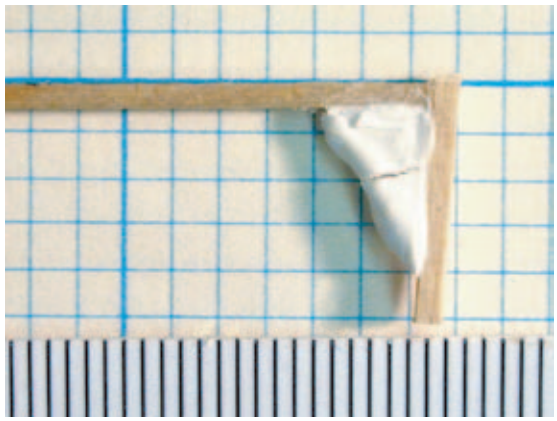
Angle tests

Angle tests were performed with the five best adhesives from the grid test: Aquazol 200, Butvar B98, Jade R, Primal WS 24, and Rhoplex B60 A. As marble dust was the best fill material, it was used as the fill material with all adhesives. The material was sculpted into a 90 degree angle formed by two pieces of 1/16th inch basswood glued at the corner with Paraloid B72.

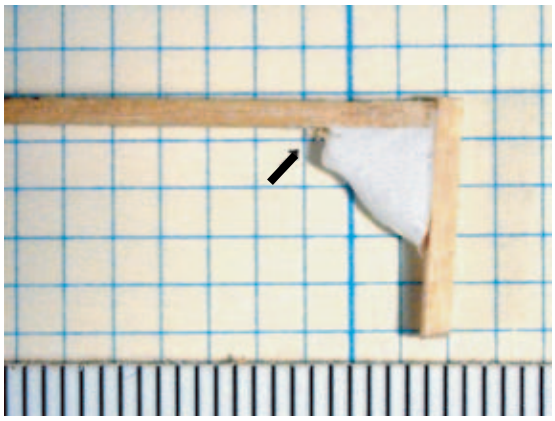
Jade R, Primal WS 24 and Rhoplex B60 A all pulled the alignment of the two pieces of basswood out of a 90 degree angle. Jade R had a less than smooth surface. Primal WS 24 cracked. Rhoplex B60 pulled away from the wood and a small piece cracked off.



Jade R 100 % with marble dust

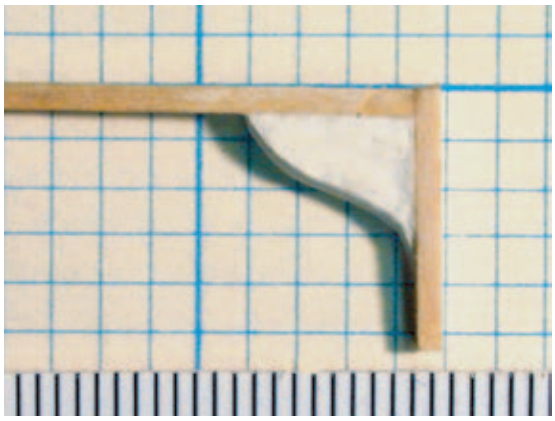


Primal WS 24 100% with marble dust

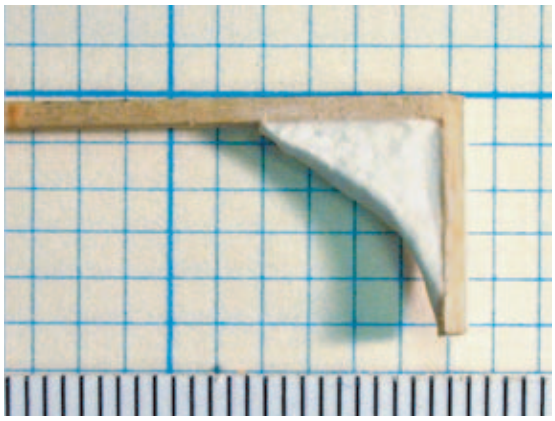


Rhoplex B60 A 100% with marble dust

In these tests Butvar B98 and Aquazol 200 performed the best. As noted from the grid test Butvar B98 was somewhat crumbly while wet, but cleaned up well with solvent. Aquazol cleaned up well with water or solvent, although it tended to pull out of the fill area until partially dry. As fill materials I believe that either Butvar B98 or Aquazol are preferable to the other adhesives tested.

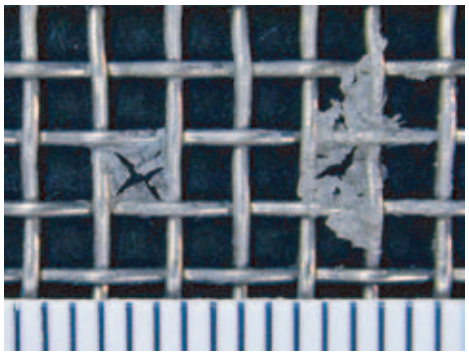


Butvar B98 @ 25% in ethanol with marble dust



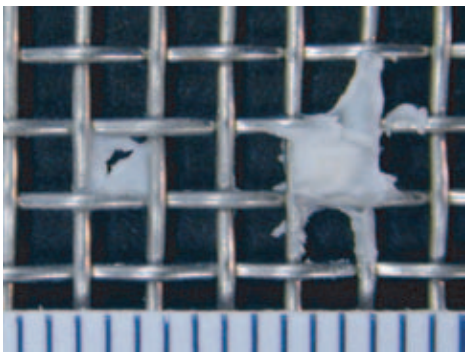
Aquazol 200 @ 50% in water with marble dust

It seems like any of the tested adhesives can be made to work as a binder for fills, with one exception. Primal (Acrysol) WS24, an acrylic colloidal dispersion in water, had too low a solids content to be of much use, shrinking badly. Golden Modeling Paste and Rhoplex B60A also shrank noticeably. Shrinkage was also seen in Aquazol 200 and Butvar B98 Cab O Sil mixtures. Both of theses products come in powder/bead form and could therefore be mixed to a higher viscosity, more Cab O Sil could also be added to the mixture.

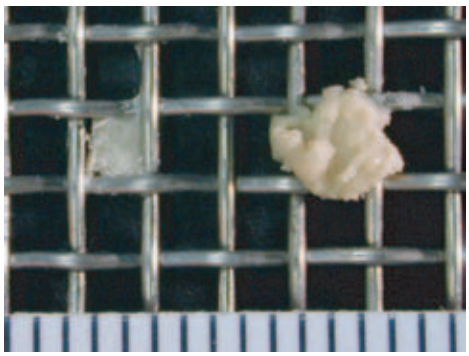


Set/Test 6/41 Primal WS 24 (100%) with Cab O Sil

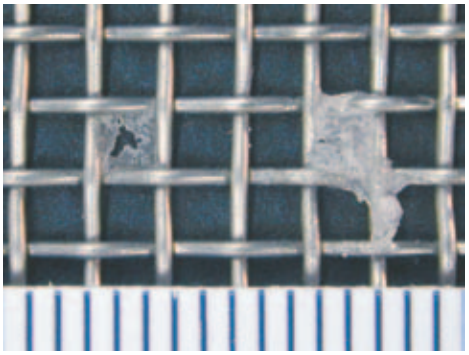
Shrinking was most noticeable with both Cab O Sil and Kaolin, even with adhesives that performed well with other fill materials, perhaps due to a smaller particle size when compared to other fills. All products would necessarily shrink somewhat due to evaporation of solvent or water.



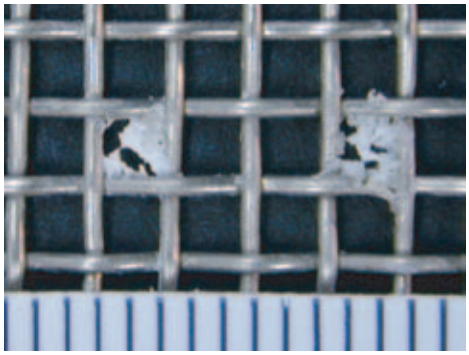
Set/Test 14/105 Golden Modeling Paste (100%) with Cab O Sil



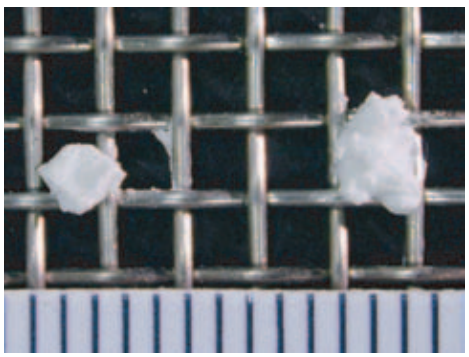
Set/Test 16/126 Rhoplex B60A (100%) with Kaolin



Set/Test 11/81 Aquazol 200 50% in water with Cab O Sil



Set/Test 12/89 Butvar B98 25% in ethanol with Cab O Sil



Set/Test 15/117 - Dap Vinyl Spackle (100%) with marble dust

Polyvinyl acetates, on the whole tended to be more rubbery when dry, and as noted before, the emulsions will tend to cross-link over time. One polyvinyl acetate was extremely rubbery - Promacto A 1023.

The DAP, of course, had no adhesion, even when filled. The ethylene-vinyl acetate, Evacon R, also lost some adhesion when filled.

Most of the glues required water or organic solvents to soften them for sculpting after drying. The use of solvents to aid in sculpting, as well as all organic solvent based products, carry the danger of resoftening the original glue joint.

The Paraloids (Acryloids), Butvar B76, Vinac and AYAF can all fall into this group. Butvar B98 and others that soften in alcohol may be slightly safer in this regard in that alcohol will redissolve the Paraloids more slowly. Paraloids are our most commonly used adhesives for the original glue joint.

Generally, water based adhesives were slightly harder to work with, drying more slowly, of course, and being somewhat messier to clean up. They can be allowed to dry slightly and then cleaned up with water or acetone. Water based products may be a danger to water soluble matrices, although a barrier layer of Paraloid B72 may be sufficient to avoid this problem.

The best possibilities as adhesives, after these very preliminary tests, in spite of showing shrinkage when mixed with Cab O Sil, were Aquazol 200 and Butvar B98. The best fill material was marble dust.

Butvar B98, although somewhat crumbly when wet, could be cleaned up well with alcohol. It remained sculptable after drying. It comes in powder form and could be mixed to higher or lower viscosities to control the fill. Butvar B98 has relatively good aging properties and remains soluble in alcohol.

The Aquazol was was fairly workable when wet and was still sculptable after drying. It comes in solid form, so can be mixed to varying viscosities, is supposed to remain soluble in water, and according to the literature, has good preliminary aging qualities. I have used this product, with marble dust as a fill material in more real-life situations and it has worked well.

I intend to continue to experiment with these and other products.

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