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ABSTRACT

Fossil reintegration is an unreliable field regarding intervention criteria and materials used according to the characteristics and requirements of specimens. Generalized use of epoxy fillers in different kinds of gaps suggest that an in-depth study on more reversible gap fillers for small to medium fossils is necessary. This paper investigates the physical-mechanical comportment of six gap fillers of three different families of resins: vinyl, acrylic and epoxy. Samples have been tested according to their working properties, aging properties, and affinity with paleontological materials. A physical-mechanical characterization has been done to gap fillers according to different parameters. Moreover, accelerated artificial aging tests have been done in all samples. After that, changes have been quantified with several analysis techniques.

Keywords: fossil gap filler; paleontological conservation; reintegration; preparation

RESUMO [in Portuguese]

A reintegração dos fósseis é um domínio não fiável se tivermos em conta os critérios de intervenção e materiais usados de acordo com as características e requisitos dos espécimes. O uso generalizado da não-reversível epoxy para preencher diferentes tamanhos de espaços em fracturas é indicador de que mais investigação é necessária para se encontrarem colas de preenchimento reversíveis para fracturas em fósseis de tamanho pequeno a médio. Este projecto estuda os comportamentos físico-mecânicos de seis tipos de colas de preenchimento de três famílias diferentes de resinas: vinil, acrílico e epoxy. Foram testadas amostras considerando as suas propriedades de manuseamento, envelhecimento e afinidade com materiais paleontológicos. Foi feita uma caracterização físico-mecânica das diferentes colas de preenchimento de acordo com vários parâmetros. Mais acresce testes de envelhecimento artificial acelerado foram feitos em todas as amostras. Depois foram quantificadas as alterações das propriedades das colas com várias análises técnicas.
INTRODUCTION

Criteria in paleontological conservation and paleontological reintegration of specimens are currently well-established amongst professionals. However, these criteria are not always respected.

Moreover, fossil reintegration is a little investigated and referenced field at this moment in Spain; even though the collection, classification, study and preparation of fossil specimens is already commonly applied (Baeza Chico et al., 2009).

As a consequence of historical paleontological excavations, fossil reintegration has been realized by professionals from different fields such as paleontologists, archaeologists, traditional preparators, museum workers, restorators or fossil owners (Thornton, 1998). All these different approaches have challenged criteria and methodologies (consciously or unconsciously) in the conservation of specimens.

Heterogeneity of materials that have been traditionally used as fillers in fossil reintegration show that more research is needed regarding methods and materials (Martínez Riera, 2015). Moreover, generalized use of epoxy resins as fillers raises the necessity to search for alternatives fillers with a higher reversibility for long term to specimens. This is because generalized use of epoxy resins for reintegration shows serious problems in reversibility when applied on specimens, and might even cause structural damage. Therefore, it is necessary to establish criteria and unify the intervention processes of epoxy resins as fillers.

OBJECTIVES

Despite the use of epoxy resins in fossil reconstruction in Spain as well as other countries, there are no specific studies that evaluate the comportment of these resins. It is necessary to evaluate what advantages and disadvantages different resins provide when used, and what possible damage may be caused in short or longer term to specimens.

There are already some studies from abroad on finding alternative fillers, such as temporary gap filling (Davidson, 2009) or reversible fillers (Haugrud and Compton, 2008). It is vital to propose alternatives in order to expand the range of options for fossil reintegration so professionals could evaluate the most suitable filler.

Under these premises, the main objective of this study is to carry out a comparison between different types of fillers with different kinds of synthetic resins of higher reversibility for small to medium fossils.

METHODOLOGY

Preparation of samples: components selection and proportions

Six different fillers from three different groups of synthetic resins have been tested: vinyl resins, polyvinyl acetate (PVAs) Rayt Standard® (Koob, 1998) and Mowital B60HH® (López Amador and Pellejero, 2007); acrylic resin, Paraloid B72® (Aberasturi Rodríguez et al., 2009); epoxy resin, Epo 150® (Lastras Pérez et al., 2007) and Araldit SV427®. Six formulas are based on polymers that have been previously used in paleontological conservation or have been suggested by other authors (Loew Craft and Solz, 1998). Powdered fossil matrix and glass microballs (0,50μ) have been added into the mixtures in several proportions to create the samples.

Thirty-two compositions (Martínez Riera, 2015) have been created before choosing the last six fillers. Four samples have been elaborated with each filler. One sample has been used as "control sample" and three of them have been tested. Measures of every sample are 35 x 35 x 10 mm. The six gap fillers are the following (see also Table 1):

- PVAs + powdered fossil matrix: filler n°1 (PV). Filler based on PVAs that originate from traditional PVAs fillers used in fossil reintegration (Koob, 1998).
- PVAs + powdered fossil matrix + glass microballs: filler n°2 (PM). This composition has been realized from filler n°1. Glass microballs have been added to the mixture to improve its physical-mechanical properties and control humidity.
- Vinylbutiral polymer + powdered fossil matrix + glass microballs: filler n°3 (M). This filler is made from the use of Mowital B60HH® in the consolidation of specimens and archeological reintegration.
- Ethylmetacrylate polymer + powdered fossil matrix + glass microballs: Filler n°4 (P). Paraloid B72® is frequently used as consolidant in paleontological conservation
Paraloid B72® is used as well in fillers with glass microballs for fossil and archeological reintegration (Larkin and Makridou, 1999). Fillers with Paraloid B72® and glass microballs have been used as reference to elaborate new fillers adding powdered fossil matrix. A proportion that has been used was 25% Paraloid B72® in acetone (Larkin and Makridou, 1999). Other authors note that the best results are obtained with solutions between 25-50% (Fox, 2001).

- **Epo 150® + powdered fossil matrix:** filler nº5 (E). This filler has been used in different proportions in reintegration of archeological specimens (Lastras Pérez et al., 2007). Commercial fillers based on epoxy resin are frequently used, therefore we decided to test the properties of one such simple commercial epoxy resins.

- **Araldit SV427®:** filler nº6 (A). Another commercial epoxy resin has been chosen in order to compare the properties between a commercial epoxy resin to other fillers used in this study.

### Table 1- Summary of fillers and components.

<table>
<thead>
<tr>
<th>Nº / Ref.</th>
<th>Proportions (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nº1 / PV</td>
<td>Rayt Standard® 95% water (55%) + fossil matrix (45%)</td>
</tr>
<tr>
<td>Nº2 / PM</td>
<td>Rayt Standard® 95% water (40%) + glass microballs (30%) + fossil matrix (30%)</td>
</tr>
<tr>
<td>Nº3 / M</td>
<td>Mowital B60HH® 10% ethanol (16%) + glass microballs (42%) + fossil matrix (42%)</td>
</tr>
<tr>
<td>Nº4 / P</td>
<td>Paraloid B72® 25% acetone (20%) + glass microballs (40%) + fossil matrix (40%)</td>
</tr>
<tr>
<td>Nº5 / E</td>
<td>Epo 150® (25%) + fossil matrix (75%)</td>
</tr>
<tr>
<td>Nº6 / A</td>
<td>Araldit SV427® (commercial product)</td>
</tr>
</tbody>
</table>

### Techniques and technical equipment used for analysis

Three analyzing techniques have been applied before and after chemical tests; electronic precision scale, optical microscopy, image analysis and spectrometry-colorimetry.

#### Electronic Precision Scale

An electronic precision scale has been used, model GRAM BH-30024 (maximum weight 300g - 0.01 g resolution). The scale has been used to take measurements and to weigh samples before and after tests in order to keep mass changes under control after accelerated artificial aging tests (Màs Barberà, 2008).

#### Spectrometry-Colorimetry

Spectrometry-colorimetry is a non-destructive analysis technique (Martínez Bazán, 2007). A Minolta CM-2600d Spectrophotometer has been used to get chromatic coordinates. Standard illuminant CIE type D56 (sunlight, 6500° K color temperature) and standard observer (10º) have been chosen as measurement conditions. Data were taken with specular component included (SCI), which minimizes the influence of conditions in the surface of the sample. Light source consists of three pulsed xenon lamps. Integrating sphere (52 mm Ø) is coated with BaSO₄. Spectrophotometer wavelength range is between 360 and 740 nm (wavelength pitch 10nm). Its reflectance range is 0 to 175% with 0.01% display resolution. Repeatability has a standard deviation of 0.1% in spectral reflectance, and chromaticity value ΔΕ * ab within 0.04 (ICD 76).

#### Optical microscopy and image analysis

The surface of the samples has been observed before and after accelerated artificial aging tests to determine changes. Images have been taken by stereomicroscope and binocular tubes. The equipment is the model Leica MZ APO25 with fiber optic illuminators and resolution from 8x to 80x. Photographs were taken by a camera adapter system with a digital camera. Images were processed by Leica Microsystems software. The photographs were taken with zoom 8x and 16x in every sample although 50x have been used in some samples after SO₂ saturated atmosphere accelerated artificial aging test.
Tests performed
Several tests have been done on every sample to determine different characteristics of the fillers. On the one hand a physical-mechanical test has been done: physical-mechanical characterization of working properties. On the other hand three chemical tests have been made simulating extreme environmental conditions: ultraviolet radiation accelerated artificial aging test, SO$_2$ saturated atmosphere accelerated artificial aging test and humidity and temperature accelerated artificial aging test.

Physical-mechanical test

Physical-mechanical characterization test of working properties. Physical-mechanical characterization by working properties of the fillers has been tested through the physical-mechanical test. This tests the parameters that a good filler must have (Fox, 2001; Lastras Pérez, 2007). The parameters are tested through the evaluation of properties of every sample (Loew Craft and Solz, 1998) by means of mechanical and physical procedures.

- Reversibility: depends on the solubility of the resin used in the composition of the filler and on the kind of solvent used to prepare the resin. Mechanical tools have been used to perform this test.
- Compatibility: compatibility of resins with specimens has been tested. Filler components have been chosen according to previous paleontological interventions and scientific studies in conservation that have shown good results.
- Structural resistance: structural resistance has been tested in each sample regarding their resistance after the drying process.
- Preparation: it is tested how simple and fast the preparation of every filler can be.
- Application: the way of application, molding, modelling and injection is evaluated.
- Drying time: time of drying is tested using the following parameters: 24 h, slow; less than 24 h, good; less than 1 hour, fast.
- Adhesion: the adhesive power of fillers.
- Volume change and cracking: observation of the volume change and cracking during cure time of samples.
- Leveling and polishing: every sample has been tested working with different tools such as a scalpel and mechanical tools of polishing (rotary tool, carborundum accessories).
- Color adjustment: color adjustment a secco has been evaluated after the drying process of the samples.
- Toxicity: depends on solvents and resins used. Companies must inform about it. It is really important to minimize toxicity for the sake of the conservators’ health and the environment.

Chemical tests

Ultraviolet (UV) radiation accelerated artificial aging test. Through the ultraviolet radiation accelerated artificial aging tests it is possible to determine what the reaction is of fillers to solar radiation and lighting inside museum rooms. UV irradiation is a cumulative degradation process in artifacts, and particularly in paleontological specimens. Light and UV exposition are registered in museum rooms by means of data loggers, and controlled by UV filters. Nevertheless, keeping UV conditions under control outside museums is more complicated because climate agents are more aggressive and variable in urban or natural environments.

Illumination conditions are recommended to specimens between 290-400 nm; direct illumination and natural light have to be avoided in museum rooms (Howie, 1979). UV radiation accelerated artificial aging tests were made to simulate environmental exhibition conditions in museum rooms. Samples have been exposed to alternating cycles of UV radiation (351 nm) for 800 hours in a QUV-BASIC QPANEL accelerated weathering tester.

Humidity and temperature accelerated artificial aging test. Relative humidity (RH) and temperature affect specimens and fillers contraction and expansion. Moreover, color is changed as well. That is the reason why physical and chemical properties of fillers are affected (Howie, 1979). In addition, saline efflorescence appears after relative humidity and temperature fluctuations in paleontological specimens, which can cause severe damage in materials (Baeza Chico and Menéndez, 2005).

Through humidity and temperature accelerated artificial aging test, extreme climatic conditions are simulated to test the properties of fillers. The test has been done in a climatic chamber DYCOMETAL MODEL CCK- 25/300 in 24 hours cycles with 60 ºC and 75% RH (cycle 1) and a
20 ºC and 20% RH (cycle 2) for one month. According to some authors, relative humidity is recommended to be between 30-60% (Baeza Chico and Menéndez, 2005) and temperatures are suggested around 23 ºC to storage (Leiggi and May, 2005).

$\text{SO}_2$ saturated atmosphere accelerated artificial aging test. It is possible to evaluate the effect of atmospheric agents in samples using the $\text{SO}_2$ saturated atmosphere accelerated artificial aging test. Resistance to sulfur dioxide has been tested because it is considered one of the most corrosive and common gases in the atmosphere. Sulfur dioxide comes from natural emissions such as volcanoes or artificial emissions (Gisbert Aguilar and Marín Chaves, 2001).

Chemicals contained in the atmosphere have accelerated the deterioration process in the last years because of the increase of industrial production and urban areas. It has become one of the most difficult alterations to keep under control. It is responsible of degradation processes such as rock sulfation (Gisbert Aguilar and Marín Chaves, 2001) and damages in paleontological specimens in museums (Howie, 1979). The test has been done using a VCK-300 MODEL DYCOMETAL chamber through the Kesternich EXPLICAR test according to DIN 50018 ($\text{SO}_2$ corrosion) with 4 cycles of duration.

RESULTS

Physical-mechanical characterization of working properties test

Different parameters have been tested to determine the best qualities of the materials (Fox, 2001; Lastras Pérez, 2007), according to their working properties (Loew Craft and Solz, 1998). Classification of each filler in every parameter of this test consists of four levels: very good/good/bad/no results.

- **Reversibility:** reversibility tests have been performed using immersion for 30 minutes in water, ethanol and acetone.
  
  Filler nº4 dissolves very well in ethanol while the solution is good and progressive in nº3. PVAs show only a light softening under ethanol immersion, whereas fillers based on epoxy resin are not reversible by ethanol immersion (Figure 1).
  
  Filler nº4 quickly dissolved in acetone. Filler nº3 has good softening and lost its consistency. Fillers nº1 and nº2 increase in volume, which makes them easier to remove with a scalpel. Fillers nº5 and nº6 do not show changes.
  
  Fillers are not reversible in water; only fillers based on PVAs show a slight softening, which makes them more pliable for a scalpel.
  
  All fillers can be removed by mechanical means. Fillers nº3 and nº4 are easy to remove by scalpels or other mechanical tools. In order to minimize damage, ethanol or acetone can be used to dissolve the filler. Nº5 and nº6 are not reversible because they are epoxy resins. Even though they can be removed by mechanical means, specimens can be affected by physical stress when epoxy resins are removed.

- **Compatibility:** PVAs fillers are used as consolidants and adhesives in fossils due to their flexibility and structural resistance (López Amador and Pellejero, 2007). Filler nº1 has been used at 95% dissolution in water. Samples with higher proportions show high water retention rates, despite the actual proportions of water being very low. Therefore, fillers based on resins that are dissolved in water are not recommended because humidity can affect the fossil. The use of fossil matrix is a guarantee of fossil compatibility because they have same composition.
  
  The same proportion as in filler nº1 has been used in filler nº2 but adding glass microballs. These have been used to reduce and control humidity. Therefore, a 55% of Rayt Standard at 95% in deionized water has been used, whereas the 45% filler is diffused with glass microballs. This reduced the humidity, however, it is still considered high.
  
  Vinylbutiral polymer is used as a consolidant in fossils because it is transparent and flexible (López Amador and Pellejero, 2007). Ethanol has been used in this test, such that no water is added to the specimens.
  
  Paraloid B72® has already been tested on many different materials in order to evaluate its stability and compatibility. It is also used in many interventions in paleontological conservation (Romero et al., 2007; González Santiago et al., 2008). Using Paraloid B72® dissolved in acetone avoids the need for water and keeps solvent impregnation under control due to acetone volatility.
  
  Despite the recommendation of Epo 150® as a filler for stone, it could deform small fossils because of the thermal reaction that is
produced during the catalysis in a non-reversible way.

Araldit SV427® is a filler used in wood reintegration and although it is used in paleontological conservation as well, the compatibility with fossil material has not been studied.

- **Structural resistance:** Filler n°1 has been used with lower adhesive volumes than fossil matrix, otherwise samples are too elastic and soft due to an excessive use of resin. Filler shape is maintained after applying manual strength.

Figure 1 – Samples after the physical-mechanical characterization of working properties test, which shows reversibility after 30 minutes in ethanol.
Structural resistance has been improved in filler nº2 because PVAs levels have been reduced due to the use of glass microballs, therefore the mixture is harder and more resistant to manual strength.

Low resin concentrations in ethanol have been used to prepare the filler nº3, in order to avoid high viscosity, glossy surface and excessive elasticity. Filler nº3 shows enough hardness to resist manual strength.

High resin concentrations have been avoided in filler nº4 because of the positive properties obtained using a mixture of fossil matrix and glass microballs instead of dissolution of the resin. Despite using high levels of resin, fillers of this concentration showed a good plasticity. Using too much resin makes fillers softer and too elastic. When resin concentrations are too low, adhesivity is reduced and fillers are useless. A balanced filler has been obtained, which is elastic enough and resistant to manual strength.

Epo 150® has high resistance properties, therefore it should only be used in very resistant specimens. Epo 150® could add more weight to the specimen so it is not recommended for large fossils. Therefore, the handling of fossils could be more difficult. It is neither recommended for medium nor small fossil bones because it could cause deformations.

Araldit SV427® also has a high structural resistance, and is recommended for big specimens. With the exclusion of Epo 150®, Araldit SV427® is lighter than the other epoxy fillers.

- **Preparation:** Necessary tools for preparation are a measuring cap, a scale and a spatula.

Preparation of PVAs fillers is easy and fast. Filler nº3 is also fast to prepare when it is dissolved immediately in ethanol.

Filler nº4 requires dissolution of the resin in acetone at least 24 h prior to use (Andrew, 2009). Paraloid B72® solution can be used for preparation instantly.

To prepare filler nº5, both components of the resin need to be mixed (resin and catalyst). The mixture can be used immediately and the preparation is fast and easy.

Araldit SV427® is prepared by mixing two components of the resin in 1:1 in mass. Preparation is easy.

- **Application:** PVAs fillers have a pasty consistency. Application can be done by molding. They have the capacity to be molded as well as to record details by taking casts. They are not recommended for injection because of the particle size and consistency. Glass microballs improve detailed casting because particle size is reduced, although viscosity is also too high for injection.

Fillers nº3 and nº4 are thick mixtures so they can be molded while drying. These fillers allow a higher detailed casting but cannot be injected.

Filler nº4 produces a film on the surface after being applied, which makes it more difficult to work with. This reaction can be solved by changing the surface tension of the filler by using some drops of methanol or ethanol while preparing the filler (Lastras Pérez, 2007).

Filler nº5 has a pasty consistency. It can be modelled and shaped with a good ability to record details. It is not suitable for injection because of its high viscosity.

Araldit SV427® is doughy, it is easy to shape and has a very high precision record when used for molding. A smoother surface of the gap filled before the filler is dried is obtained when wetting the spatula in acetone or water.

- **Drying time:** PVAs fillers have similar properties during drying period although drying time in PVAs fillers with glass microballs is shorter. Total drying time is slow, over 24 hours, when we allowed natural drying, although this depends on the climate conditions. If the drying time is accelerated through artificial heating, a stratification in the samples appears, making drying of internal parts of the samples more difficult. When samples are used by molding, the drying is very slow and irregular, which is increased by using silicon molds that isolate the internal part from the environment (Figure 2). Slow drying results in high humidity for a long time, so that PVAs fillers cannot be recommended for application on fossil bones.

Drying time in filler nº3 is good. This filler allows time enough to have a good application and work it in. Drying time depends on solvent volatility, although this is conditioned by climate conditions.

The drying time of filler nº4 is good. Filler nº4 has good working properties together
with drying time, and can be kept under control by adding other solvents with lower volatility such as methanol or ethanol (Lastras Pérez, 2007).

Drying time in filler n°5 is slow because it depends on the catalysis resin process (24 hr at least). The same happens to Araldit SV427®. Time could be variable depending on atmospheric conditions.

- **Adhesion**: PVAs fillers show very good adhesive properties. They show high resistance and elasticity (López Amador and Pellejero, 2007). Mowital B60HH® and Paraloid B72® also display good adhesive properties and good elasticity. Paraloid B72® at 20% concentration gives fillers good adhesive properties to medium specimens. However, epoxy fillers show high adhesive power and are very resistant so they are recommended to heavy and big fossils.

- **Volume change and cracking**: PVAs fillers have similar properties related to volume change during the drying process. Volume change is medium to high, although the humidity on the mixture preparation process has been controlled by adding glass microballs (Figure 3). When water levels are higher, the volumetric change is higher too, however, cracking of the fillers decreases, which gives better cohesion to the mixture. Larger amounts of glass microballs therefore avoids cracking of the filler and reduces the change in volume. Volume change in fillers n°3, 4, 5 and 6 is virtually null or imperceptible to the human eye. No cracking of the surface has been observed either.

- **Leveling and polishing**: PVAs fillers, due to their plastic surface, can be leveled cutting the surface with a scalpel, although the surface will be irregular and it will be difficult to have a smooth surface. Sanding or grinding, either by manual means with sandpaper, or by mechanical means with a micromotor does not work, because fillers have a plastic surface. Fillers n°3 and 4 have similar working properties. Mechanical tools (scalpel, rotatory tool) can be used on the surface. Surface sanding is easy by means of sandpaper or polishing with electrical tools. The surface can be softened to work easier with proper solvents.
Filler nº5 is very difficult to level with a scalpel because the filler is too hard. Filler nº5 can be modeled and polished with mechanical tools, although this could produce mechanical stress to the specimens. Levelling is recommended before drying. Araldit SV247® can be carved with a scalpel or other mechanical tools. This filler can be sanded with sandpaper or a rotatory tool.

- **Color adjustment:** PVAs fillers do not allow retouching with watercolor or glazing with water due to their plastic surface. However, adjustments can be made through other acrylic-based paint or other solvents. Other fillers allow color retouching with any water-based paint or other solvents.

- **Toxicity:** PVAs Rayt Standard® is a non-harmful and non-hazardous product. Furthermore, the common solvent used is deionized water, which is a harmless product. Fillers nº3 and 4 will be more toxic due to the use of ethanol and acetone as solvents. The toxicity of fillers based on Epo 150® and Araldit SV427® is determined by the composition of the resins, which must be listed by the brand.

All fillers have a good leveling, polishing and color reintegration (Figures 4 and 5) except PVAs fillers, due to their plastic surface. They cannot be colored with watercolors. PVAs fillers experience a huge change in their volume compared to other fillers. Drying is regular in every gap filler excepting PVAs fillers because they show a stratified drying. Epoxy fillers display great adhesion power.

### Ultraviolet radiation accelerated artificial aging test

General rates of mass loss have been registered between 0,43 g and 0,10 g. Loss in mass is probably due to the loss of humidity of fillers during the test. Filler nº5 shows the best properties with any variation. Loss in mass could be related to changes of physical-mechanical properties after long expositions to UV radiation (Table 2).

There are no relevant changes in the surface of the samples after comparing the optic microscopy images before and after the UV radiation accelerated artificial aging test.

There are significant changes in colorimetric coordinates. Colorimetric analysis (Figure 4) shows visible changes $\Delta L^*$ (4,56) and $\DeltaE_{ab}^*$ (5,01) of filler nº4. Filler nº3 reveals equal deviations although rates are lower. PVAs fillers present similar results, although rates are

### Table 2 - Rates of mass loss: Ultraviolet radiation accelerated artificial aging test (mass in g)

<table>
<thead>
<tr>
<th>FILLER</th>
<th>Nº OF FILLER</th>
<th>AVERAGE CHANGES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>PV</td>
<td>14,1</td>
<td>12,9</td>
</tr>
<tr>
<td>PM</td>
<td>18,3</td>
<td>18,8</td>
</tr>
<tr>
<td>P</td>
<td>20,9</td>
<td>21,3</td>
</tr>
<tr>
<td>M</td>
<td>17,8</td>
<td>16,4</td>
</tr>
<tr>
<td>E</td>
<td>20,3</td>
<td>21,3</td>
</tr>
<tr>
<td>A</td>
<td>10,31</td>
<td>7,6</td>
</tr>
</tbody>
</table>
bigger in $\Delta L^*$ (8,20) and $\Delta AEab^*$ (9,68) in the gap filler with glass microballs. Epo 150® filler has the most stable rates with visible changes in $\Delta L^*$ (2,29) and $\Delta AEab^*$ (3,75). The most unstable filler is Araldit SV427®, which shows visible changes in all the parameters.

There are relevant visible changes in chroma ($C^*$) rates in fillers based on PVAs and Araldit SV427®. Araldit SV427® shows in $\Delta C^*$ a maximum of -8,82 units CIELAB. There are also visible changes in filler n°4 (-2,05) although changes are not as important as in Araldit SV427®. All fillers change chroma from weak (before test) to greyish.

The Araldit SV427® reveals visible changes in color tone ($h^*$); the filler changes from orange tone (56,30) to orange-red (49,76).

Paraloid B72® and PVAs samples do not show changes regarding color tone ($h^*$). Tone is orange-yellow before and after the test. Fillers n°3 and n°5 maintain also a stable tone yellow-orange. Fillers n°3 and n°5 reveal also a weak chroma ($C^*$) without any visible changes.

There are visible changes only in Araldit SV427® on rate $L^*$. Data conversion reveal that brightness has a medium level before ultraviolet radiation accelerated artificial aging test but it shows a light level after the test.

SO$_2$ saturated atmosphere accelerated artificial aging test

PVAs fillers do not show any relevant changes in mass (0-0,07 g) after this test, the same as epoxy gap fillers: Epo 150® (0 g) and Araldit SV427® (-0,03 g). Paraloid B72® (0,3 g) and Mowital B60HH® (0,9 g) fillers show the highest registered data of mass loss. This is probably related to a cohesion loss during the test and, consequently, the loss of material during the SO$_2$ saturated atmosphere accelerated artificial aging test (Table 3).

Relevant changes have been registered in colorimetric coordinates (Figure 5). The most stable are the gap fillers based on Paraloid B72® and Mowital B60HH®. They register visible changes in $\Delta AEab^*$ of 3,61 and 2,8 respectively. Filler n°4 has changes in $\Delta L^*$ of 3,21. Colorimetry analysis reveals the biggest change in the epoxy gap fillers. Araldit SV427® is the most variable in colorimetry with maximum rates in $\Delta AEab^*$ of 21,78 and negative rate in $\Delta a^*$ of -7. Filler n°5 has high rates in $\Delta L^*$ (17,65) and $\Delta AEab^*$ (17,9). There are negative values in rates of $\Delta b^*$ (-2,81) and $\Delta C^*$ (-2,81). Fillers based on PVAs show similar changes. PVAs fillers with glass microballs have higher values in $\Delta L^*$ (9,41) and $\Delta AEab^*$ (10,77), although PVAs fillers without glass microballs show higher rates in $\Delta b^*$ (-5,07) and $\Delta C^*$ (-5,23).

The PVAs filler with glass microballs shows significative changes in chroma ($C^*$; -5,23). Fillers n°3 and n°5 also show visible changes in chroma ($C^*$) although they are lower and they change from weak chroma to greyish.

Araldit SV427® has an orange tone ($h^*$) (57,81) that changes visibly to an orange-yellow tone (78,83) with $\Delta h^*$ of 21,01 units CIELAB. However, Paraloid B72® and PVA samples have orange-yellow tone. Fillers n°3 and n°5 have yellow-orange tone that are stable before and after the test.

Fillers based on Paraloid B72® and PVAs show medium brightness on rate $L^*$. Fillers n°3 and n°5 are light. However, Araldit SV427® reveals brightness changes from medium to light.

Analyses using optic microscopy do not reveal general relevant changes before and after this test. However, there are changes in epoxy gap fillers: Araldite SV427® (Figure 6) and Epo 150® (Figure 6). These changes probably result from the resin characteristics, the fossil matrix used in the mixture or the products added during the SO$_2$ saturated atmosphere accelerated artificial aging test. In filler n°5 the test probably

Table 3 - Rates of mass loss: SO$_2$ saturated atmosphere accelerated artificial aging test (mass in g).

<table>
<thead>
<tr>
<th>FILLER</th>
<th>Nº OF FILLER</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>AVERAGE CHANGES</th>
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</tr>
<tr>
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<tr>
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<td>-</td>
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<tr>
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<tr>
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<td>-</td>
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<tr>
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<td>9,7</td>
<td>7,9</td>
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</table>
shows efflorescence salts (Figure 6). These presumed efflorescence salts appear also in Araldit SV427® as white spots on the surface (Figure 6). These spots need to be analyzed in further tests. Analysis using optic microscopy also shows that porosity has increased and new cracks have appeared in Mowital B60HH® fillers (Figure 7).

**Humidity and temperature accelerated artificial aging test**

PVAs fillers are really stable after the humidity and temperature accelerated artificial aging test. They register mass changes of 0 g and 0,07 g. Epo 150® filler appears stable after mass variation analysis, whereas Araldit SV427® has the highest mass change (0,27 g), which may be because of humidity absorption during the test. Filler nº4 (0,1 g) does not show any relevant changes. Filler nº3 (-0,03 g)
Table 4 - Rates of mass loss: Humidity and temperature accelerated artificial aging test (mass in g).

<table>
<thead>
<tr>
<th>FILLER</th>
<th>Nº OF FILLER</th>
<th>AVERAGE CHANGES</th>
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</thead>
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<tr>
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<td>2</td>
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<tr>
<td></td>
<td>Before</td>
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</tr>
<tr>
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<tr>
<td>PM</td>
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<tr>
<td>P</td>
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<tr>
<td>M</td>
<td>20,2</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>27,2</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

shows a low mass loss, which can be considered irrelevant (Table 4).

Colorimetry analysis (Figure 8) shows important changes in several samples. Epo 150® is the most stable filler, there are no visible changes in its parameters. The biggest changes appear in Araldit SV427®, with negative visible registers in rates Δb* (-5,91), ΔC* (-5,82), and Δh* (-6,54) and positives in ΔAEab* of 6,42. PVAs fillers have similar results with almost identical quantities and figures (ΔAEab*: 6,62).

Filler nº4 is stable. It only reveals visible changes in ΔAEab* with 2,33. Filler nº3 has also a stable comportment similar to filler nº4. Rates have visible changes in ΔL* (2,08) and ΔAEab* (2,89).

There are visible changes in chroma (C*) in PVAs fillers and Araldit SV427® that change from weak chroma before the test to greyish with maximum ΔC* of -5,82 CIELAB units. In addition, in the Araldit SV427® sample, visible changes in tone (h*) go from orange (56,30) to orange-red (49,76).

Fillers nº1, nº2, and nº4 do not show visible changes. They maintain their orange-yellow tone (h*) before and after the test. The same happens with the fillers nº3 and nº5, which maintain tone (h*) in yellow-orange.

Fillers nº3, nº4, and nº5 do not reveal any visible changes in chroma (C*). They show weak chroma (C*) before and after the test.

L* rate reveals medium brightness in all fillers, however filler nº3 shows a light rate.

Optical microscopy image analysis does not reveal any change on the surface of the samples tested before and after humidity and temperature accelerated artificial aging test.

Figure 6 - A,B) (x16) possible salt efflorescence in Epo150® filler after SO₂ saturated atmosphere accelerated artificial aging test. C,D) Araldit SV427® before and after SO₂ saturated atmosphere accelerated artificial aging test where what seems to be salt efflorescence appears in the image taken after the test.
Figure 7 - A) (16x) shows the sample before the test. B,C) higher porosity and cracks after SO$_2$ saturated atmosphere accelerated artificial aging test in the Mowital B60HH® filler.

Figure 8 - Graphic of increases (SCI) $\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta AEab^*$, $\Delta C^*$, $\Delta h^*$ after the humidity and temperature accelerated artificial aging test after processing colorimetric data.

CONCLUSIONS

The best results have been obtained with Paraloid B72® and Mowital B60HH® fillers in general rates. They have good working properties and they are stable during the SO$_2$ saturated atmosphere accelerated artificial aging test, and also do not show any relevant changes compared to other fillers tested. Moreover, they possess high reversibility and resistance, which makes them ideal to apply to medium to small fossils. They also do not add high levels of humidity related to other fillers tested, and humidity is also under control.
Mowital B60HH® shows decohesion, revealed by its mass loss, cracking and porosity in samples after the SO$_2$ saturated atmosphere accelerated artificial aging test. This decohesion can be fixed by adding a larger quantity of resin during the preparation. Application of Paraloid B72® filler can be improved by using different solvents during the preparation, such as ethanol (Lastras Pérez, 2007). These improvements will be developed in future studies.

Epoxy gap fillers should be used only with large and resistant specimens because they are irreversible, due to the high adhesive power and high resistance they possess. There are no significant changes in mass, however, it is important to highlight that Epo 150® filler does not show any mass change after the accelerated artificial aging tests. Therefore, it can be stated that this is the most stable filler regarding mass changes over time. Despite these properties, Epo 150® fillers do add more weight to large specimens, which makes the handling of specimens more difficult. Furthermore, epoxy resins are really unreliable regarding chromatic changes after accelerated artificial aging tests. Araldit SV427® is the most unstable filler regarding the SO$_2$ saturated atmosphere accelerated artificial aging test and the UV radiation accelerated artificial aging test, compared to other fillers. It is also important to note that epoxy fillers appear to generate salt efflorescence after SO$_2$ saturated atmosphere accelerated artificial aging test. Also, it has to be noted that Araldit SV427® is a commercial preparation that could be changed by the producer, so mixture components could change at any moment (Loew Craft and Solz, 1998).

PVAs fillers are stable regarding changes in mass. PVAs filler without glass microballs register a mass change of 0, while PVAs filler with glass microballs added register a change in mass of 0,07 and -0,07. This could be due to the fact that glass microballs destabilize the filler regarding mass change. However, glass microballs do stabilize the filler regarding SO$_2$, humidity and temperature. These fillers display large problems of working properties: they give specimens high humidity levels because of their long drying periods, and it is also difficult to polish and level them. In addition, they are chromatically instable after UV radiation, and the SO$_2$ saturated atmosphere and humidity and temperature accelerated artificial aging tests.

Using an interlayer is recommended (López Amador and Pellejero, 2007) to avoid direct contact between gap fillers and specimens. In this way the treatment will be more reversible and also, fossils will be protected from salt contamination. In addition, purification of the fossil matrix used in the samples is proposed for future analysis.

Despite generalized use of Paraloid B72® and epoxy resins as a base of fillers in fossil reintegration, there are no studies yet where compatibility of gap fillers with different fossils is valued. Moreover, no study noted that epoxy resins do not keep conservation principles because they are not reversible and have a huge grade of yellowing.

It is important to consider the toxicity of gap fillers. Future research looking for alternative solvents is proposed, which are less harmful for conservators and the environment (Larkin and Makridou, 1999).

In conclusion, research results show factual data that have to be valued by conservators in order to select the best materials to be used during conservation process.

REFERENCES CITED


Additional images and material can be downloaded at http://www.jpaleontologicaltechniques.org/