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Ilaria Forno is a graduate of Materials Engineering from Polytechnic University of Turin. Now she is studying for a PhD in Industrial Production and Design Systems, developing a thesis sponsored by the Consorzio Promoteo regarding the precision casting of precious metals with an analysis of materials and methods.

In recent years, the gold and jewellery business has shown a gradual interest in rapid prototyping techniques as an element that could meet increasingly "extreme" design requirements.

Although direct casting models can already be produced with rapid prototyping, this potential is not yet being taken full advantage of. The reason could be the lack of detailed information on the materials and the correct processing and treatment techniques. Understanding the characteristics of the material, in fact, plays a vital role in achieving a high quality product.

A number of studies have been conducted in the past on production parameters, the development of materials able to adapt to the properties of resins and the search for "tricks" and practical indications for processing them. It is, however, necessary to make an even further assessment of the criticalities, not only in the production phase of resin models (slicing and model orientation, accuracy, UV reticulation) but also throughout the entire productive cycle (especially in regard to oxygen "supply" during cylinder baking and residue evacuation).

Moreover, other external factors that can influence the reaction of the resin are to be taken into consideration, like aging, packaging, cleaning, handling, etc. Lastly, another aspect to bear in mind concerns resin dilation during cylinder baking.

The difference between one resin and another mainly lies in their chemical composition. There are products on the market that range from resins that are very similar to waxes to entirely plastic products but they can typically be distinguished by their greater or lesser propensity for direct casting.

Therefore, the chemical-physical characteristics of the material used must be assessed due to their considerable effect on the final results in terms of casting quality.

The aim of this work is to analyse resins for rapid prototyping with a scientific approach, firstly by gathering the relative information on the thermal, physical and mechanical behaviour of the material and then by putting this acquired knowledge into practice, correlating the characteristics of the material and the correct procedure to use.

Direct casting of resin by rapid prototyping: the importance of a scientific approach in creating quality products

Introduction

Due to their considerable advantage in terms of design and modelling cost reductions, rapid prototyping techniques are currently being widely practiced. Moreover, they make creating complex geometrical shapes relatively easy and reduce production times [1,2].
The gold and jewellery business is therefore a perfect field in which to apply this type of technique because of the constant need to cut the time it takes to produce innovative, extremely personalised and unique items[3].
The direct casting of resins by prototyping could therefore be an interesting solution to these needs. Rapid prototyping has great innovative potential that is still not being fully exploited in the gold and jewellery field. Finding the right processing conditions for the direct casting of resins could therefore lead to creating high quality products with a unique and extremely personalised design.
Various studies have been carried out in the past to understand how resins are affected by prototyping in terms of the final micro-fusion result, to solve the problems of removing the resin object from the mould and to obtain a good surface quality of the cast and polished items[5,6].
These considerations have led to several studies on using rapid prototyping resins in the traditional micro-fusion process [7,8,9]. The traditional process has been modified a number of times in the past in order to adapt it to the use of resins. Despite the effectiveness of some of these tests, prototyping resins are still not being used to their full potential, mainly because companies prefer not to make too many drastic modifications to the process so that they can take advantage of using resins and waxes in the same working situation. However, in order to reach this aim, it is necessary to understand the behaviour of the various materials involved in the process and the way they interact. The purpose of this work is to provide information from a scientific point of view on the thermal and chemical behaviour of resins and to apply this knowledge to improve casting tests.

Thermo-chemical analysis definition

In order to conduct a thorough analysis in terms of this particular research, the materials involved in the process were characterised and casting tests were carried out. Information on the thermal and physical nature of the materials provides an understanding of the mechanisms that take place during the process[10], while experimental casting tests aim at translating, at a macroscopic level, what the scientific analysis revealed.

Various resins from several producers were examined for rapid prototyping.

Fig. 1 Examples of objects produced in resin using different methods of rapid prototyping

The properties of polymeric materials like resins, and also the more traditional waxes, are strongly correlated to the chemical nature of the material. The chemical analysis of a material is usually conducted using spectroscopic techniques[11].

Infrared spectroscopy, using the principle of absorption, measures how molecules absorb specific frequencies which are characteristic and particular to their nature. This analysis gives the various infrared spectrums of the polymers. These are then compared to a spectrum database so that the different polymeric components of the analysed material can be identified.

Another key point for obtaining a complete characterisation of a resin is the analysis of its thermal behaviour. Thermal analysis evaluates the effect that temperature has on the polymer's intrinsic properties so that the working temperature, the glass transition temperature, the softening point (or melting point depending on the material's degree of crystallinity) and the behaviour of the degradation can be determined. It is therefore possible, by means of calorimetric analysis, to understand the thermo-hardening or thermo-plastic nature of a polymer.

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique which measures the difference in heat required to analyse, in a given temperature interval, a sample of material by comparing it to a reference material. When the sample undergoes a physical transformation (e.g. a phase transition) the instrument will record a difference between the heat of the sample and the heat of the reference material. The process is defined as exothermic or endothermic depending on the difference in heat flow between the sample and the reference material needed to maintain both products at the same temperature. If the heat flow on the sample is less than on the reference material, then the process is exothemic. If it is more, then it is endothermic.

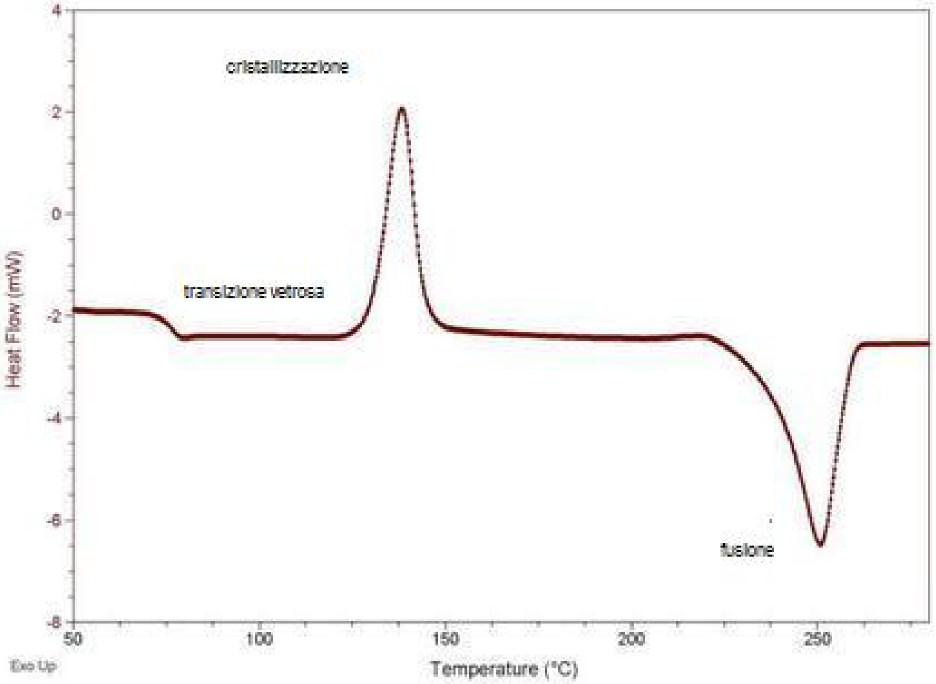

Fig. 2 Typical DSC analysis of a plastic material showing an example of peak exothermic crystallisation, peak endothermic melting and a change of curve due to glass transition.

The main purpose of DSC analysis is to determine the melting point, the glass transition temperature, the specific heat and the crystallisation kinetics.

Another important process is weight loss during temperature, a typical reaction of polymers after degradation and loss of solvents and monomer residues. This phenomenon is analysed by thermo-gravimetric analysis (TGA), a test that determines changes in weight correlated to variations in temperature. The technique is mainly used to determine degradation temperatures, the amount of humidity absorbed and the relationship between the organic phase and the inorganic phase.

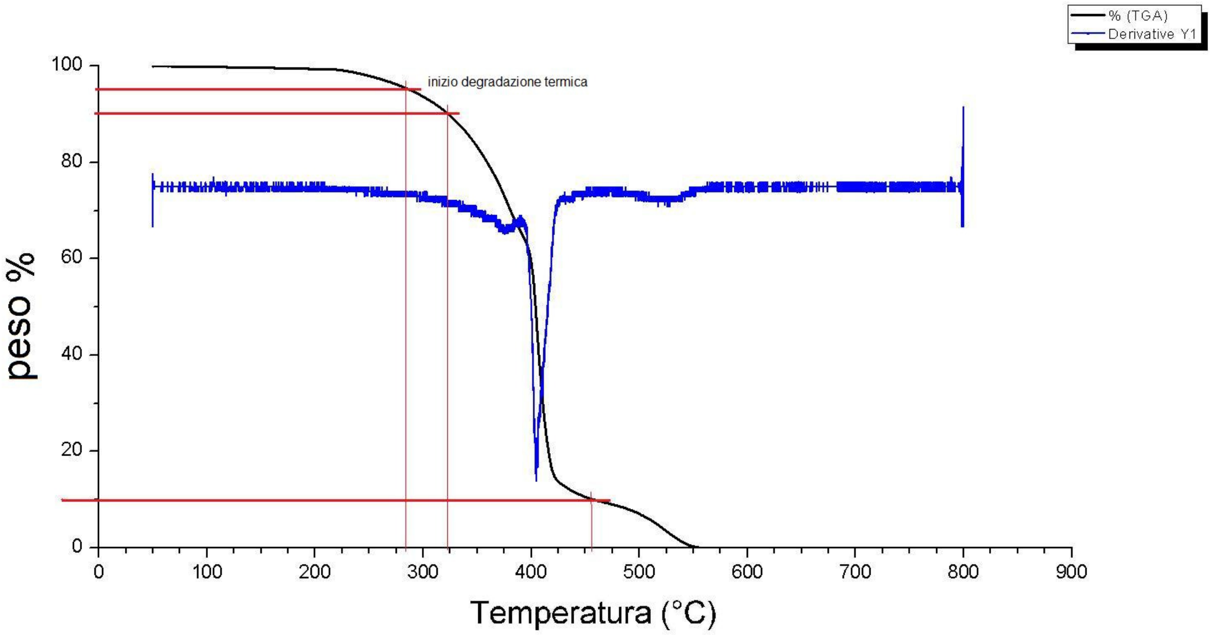

Fig. 3 Typical graph resulting from TGA analysis. It is usually established that thermal degradation begins when weight loss equals 10%. The derivative blue line represents the weight loss peak.

In order to completely characterise the thermal properties, changes in dimension correlated to changes in temperature must also be examined. The material's tendency to expand as the temperature rises can be measured by deriving a thermal expansion coefficient obtained by a ratio between volume and temperature variation. The test result gives the parameter α_l, defined as the linear thermal expansion coefficient [°C^{-1}] :

$$\frac{\Delta l}{l_0} = \alpha_l \cdot \Delta T$$

l_0 *and* l_f respectively represent the initial and final lengths at changes in temperature going from T_0 to T_f. .
Heating (or cooling) affects the dimensions of all objects with a change in volume equal to:

$$\frac{\Delta V}{V_0} = \alpha_v \cdot \Delta T$$

.

Assuming that the material is isotropic, $\alpha_v = 3\alpha_l$.

Thermal expansion tests were carried out on the resins both in the longitudinal and transversal directions, depending on the construction orientation, in order to assess any anisotropic behaviour of the material or in the process of creating the model.

Thermo-chemical analysis results

Applying a scientific approach to the physical and chemical characteristics of polymeric materials provides information on their properties and thus leads to a better understanding of what happens during the direct casting of resins.
Firstly, the composition and thermal and physical behaviour of the various materials were analysed in order to define the chemical characteristics of the material being examined.
In particular, with a view to understanding how resins can adapt themselves to processes that are traditionally studied for the use of waxes, it was necessary to analyse both waxes and resins and then compare the chemical and physical characteristics of both materials.
Initially IR analyses were carried out to obtain a spectrum with which to identify the functional groups in the material.

From the micro ATR analysis conducted on the various commercially available waxes, it was noted how the IR spectrum was substantially the same. The example below shows the spectrums relating to two commercial waxes examined for filigreed objects (pink line) and for general use (blue line). Intense bands can be observed at 2950 cm^{-1} and at 1460 cm^{-1} ^{e} and a band of average intensity at about 725 cm^{-1}.

The peaks at 2950-2800 cm^{-1} are due to the stretching vibrations of the CH_2 groups (symmetrical and asymmetrical stretching respectively). A less intense band with a higher wavelength shows the presence of a small quantity of CH_3 groups. The band at 1460 cm^{-1} is due to the bending vibrations of the CH_2 groups.

They are typical polyethylene paraffin spectrums and there is no significant difference in terms of composition between the different materials.

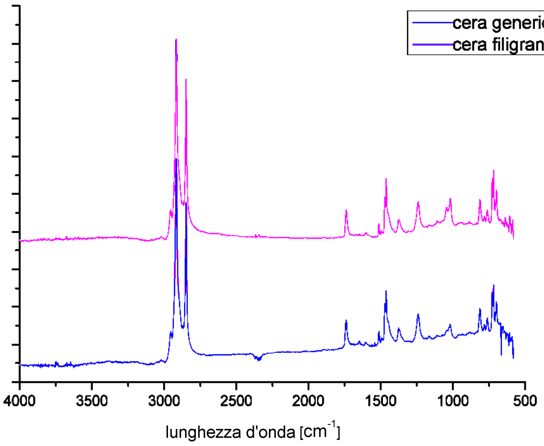

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Fig. 4 IR spectrum of commercial waxes: comparison between generic wax (blue) and wax used specifically for filigreed objects (pink).

A further analysis was conducted in the same way on prototyping resins. In general the IR spectrum of the resins showed a more complex structure. In the example in figure 5, a medium-high intensity band can be seen in the 1810-1700 cm^{-1} and 1100-1050 cm^{-1} regions, which is typical of the epoxy resin spectrum. The presence of bands corresponding to the CH_2 groups is linked to the presence of ramified structures.

Comparing the two spectrums, it can be observed how resins from the same family can show slightly different spectrums.

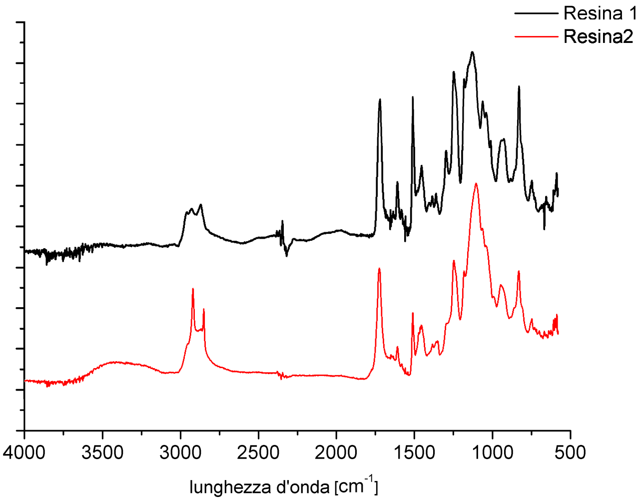


Fig. 5 IR spectrums of commercial resins belonging to the same family of polymers.

Several commercial waxes and resins were analysed using TGA analysis conducted in air with a thermal ramp of 10°C/min from 50 to 800°C.

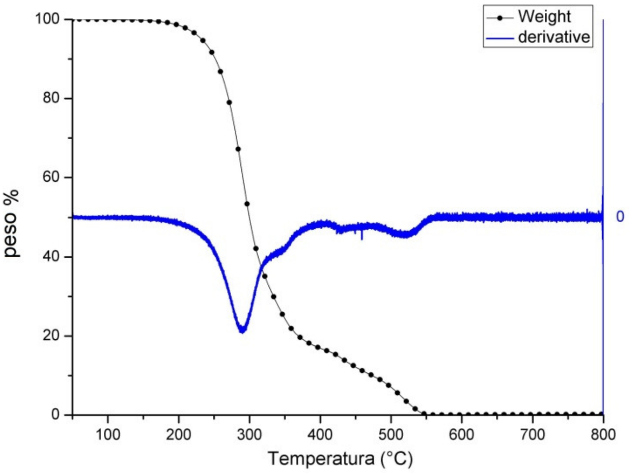


Fig. 6 TGA analysis of a commercial wax

Thermo-gravimetric analysis conducted on waxes showed that their thermal degradation leaves no solid residue. Weight loss resulting from thermal decomposition started at 150°C. At 350°C about 80% of the initial weight has already been lost. This information gives a complete picture of the behaviour of the material and helps in understanding what happens when ideal loss of weight in carats does not occur, for example, if the process is hindered by an inappropriate filling of the parts.

TGA analysis carried out on resins generally showed greater heat resistance than waxes. Degradation (90% of residual weight) started at a range between 300° and 375°C and ended around 425-550°C . For the majority of materials, the graph shows a rapid loss of weight around 450°C. Total material degradation occurs at 580-600°C.

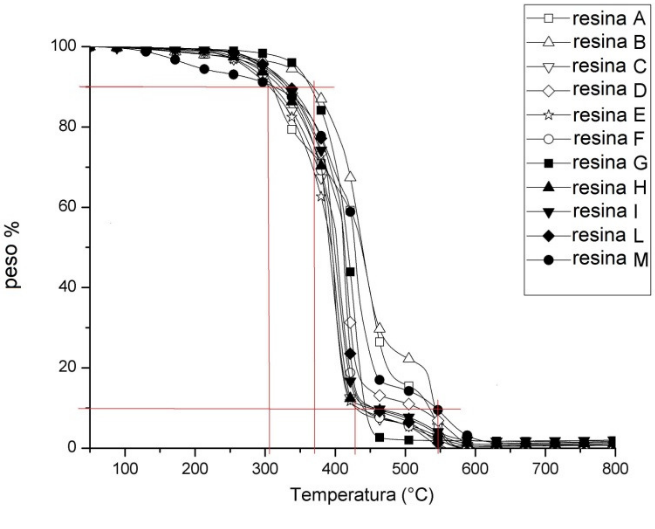


Fig. 7 TGA analysis of a series of rapid prototyping resins.

Alongside the TGA analysis, various commercial waxes and resins were also analysed using DSC equipment to verify their melting behaviour and to characterise the temperature interval as melting occurred.

The DSC analysis for waxes showed a melting peak around 60°C with slightly different values for the two materials. This behaviour difference can be explained by the different proportions of common elements within their composition, which is highlighted in the IR spectrum.

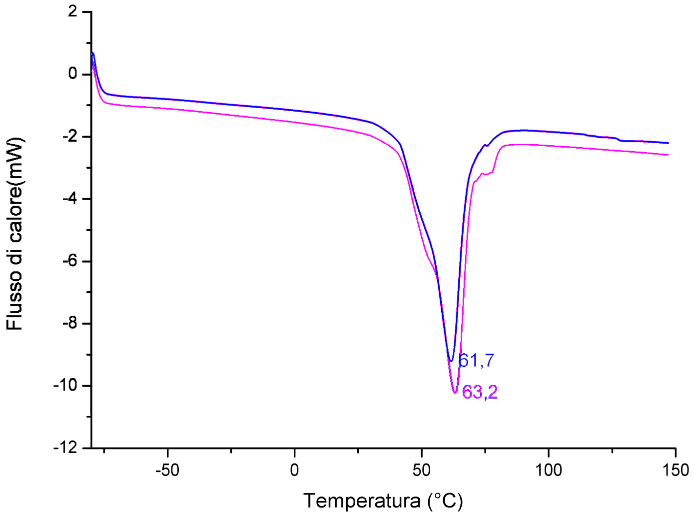


Fig. 8 DSC analysis of commercial waxes: comparison between generic wax (blue) and specific wax for filigreed objects (pink).

The DSC analysis carried out on various resins showed different behaviours due to the characteristics of each material. For example, resin F has two partially overlapping peaks due to the melting of two distinct crystalline phases at 90°C and 115°C, while resin M has no visible peaks but a curve variation can be seen due to a glass transition from solid to liquid at around 60°C.

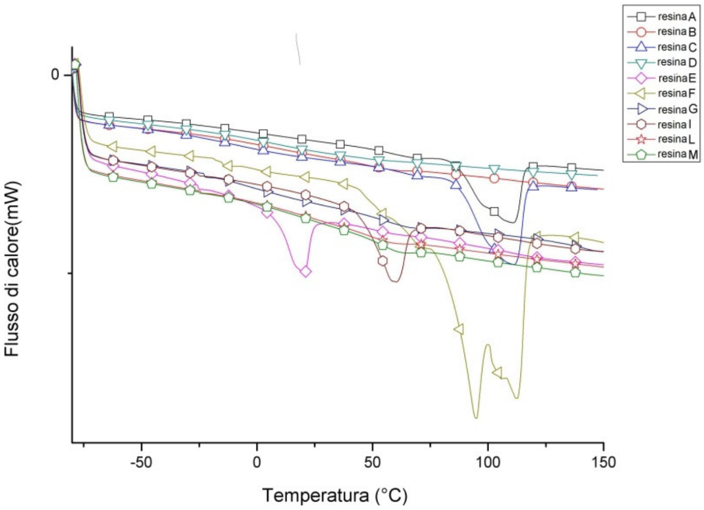


Fig. 9 DSC analysis of various commercial resins.

The evaluation of these figures provides some indications on resin behaviour.

Resins can be substantially divided into two main groups. Some rapid prototyping materials show melting peaks relating to the originally waxy crystalline components and appear between 30 and 100°C depending on the degree of polymerisation. The other observable behaviour is due to a totally amorphous composition which leads to the absence of melting peaks. Furthermore, it is also possible to make some consideration regarding thermal decomposition. Generally speaking, these materials are not subject to thermal degradation until 150°C and are totally degraded at temperatures of over 600°C. The diagrams below give a detailed picture of the behaviour of some model systems.

Figure 10 A shows the TGA and DSC analyses of a material that starts to degrade thermally at 340°C, with a 10% loss of its initial weight at 360°C. Weight loss reaches 90% at 450°C due to degradation but there is no inorganic residue when degradation is complete.
Considering its behaviour on heating, the DSC analysis shows the formation of a stable crystalline phase above -20°C and a melting peak of low-melting oily elements at 15-20°C .

Other types of behaviour can be observed: material B, for example, shows a more staged degradation due to the heterogeneity of the material with an initially slow weight loss that begins at 350°C, while observation of its behaviour during heating, shows a curve variation due to glass transition (amorphous behaviour) around 60°C.

Material C shows a clear melting peak of its low-melting components at 25°C and a regular thermal degradation curve with weight loss starting at 200°C and reaching 90% at 420°C, thus proving that its behaviour towards heat is more sensitive than the other materials.

Lastly, material D shows less heat resistance compared to the other materials with a thermal degradation starting at 150°C and a rapid loss of weight. In fact, the material loses 90% of its initial weight at 300°C. The DSC analysis highlights the presence of two different crystalline fractions with partially overlapping melting peaks at 90°C and115°C.

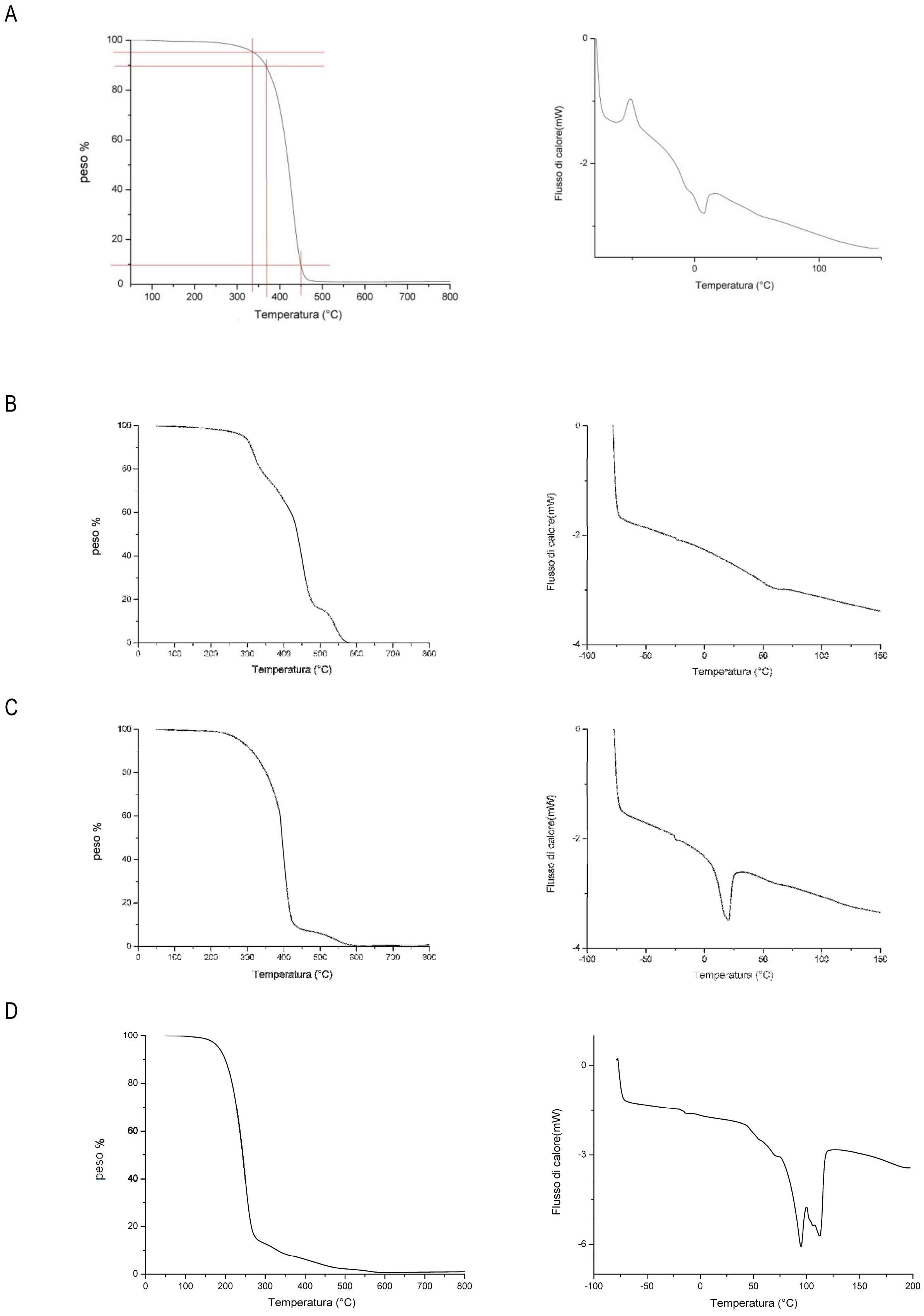


Fig. 10 TGA and DSC analyses conducted on various commercial resins.

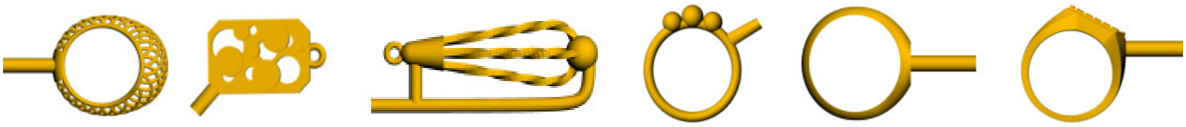
Casting tests

For a more precise interpretation of the information obtained from analysing the materials, casting tests were then performed. A standard casting tree was designed and created containing both solid and filigreed objects with thick and thin sections and curved and flat surfaces.

The pieces consisted of three different pendants reproducing filigreed items (heart pendant), flat surfaces (dog-tag pendant) and a variable section (dropper pendant) as well as five rings with varied sections ranging from very fine (cage rings) to solid models (rectangular signet ring).

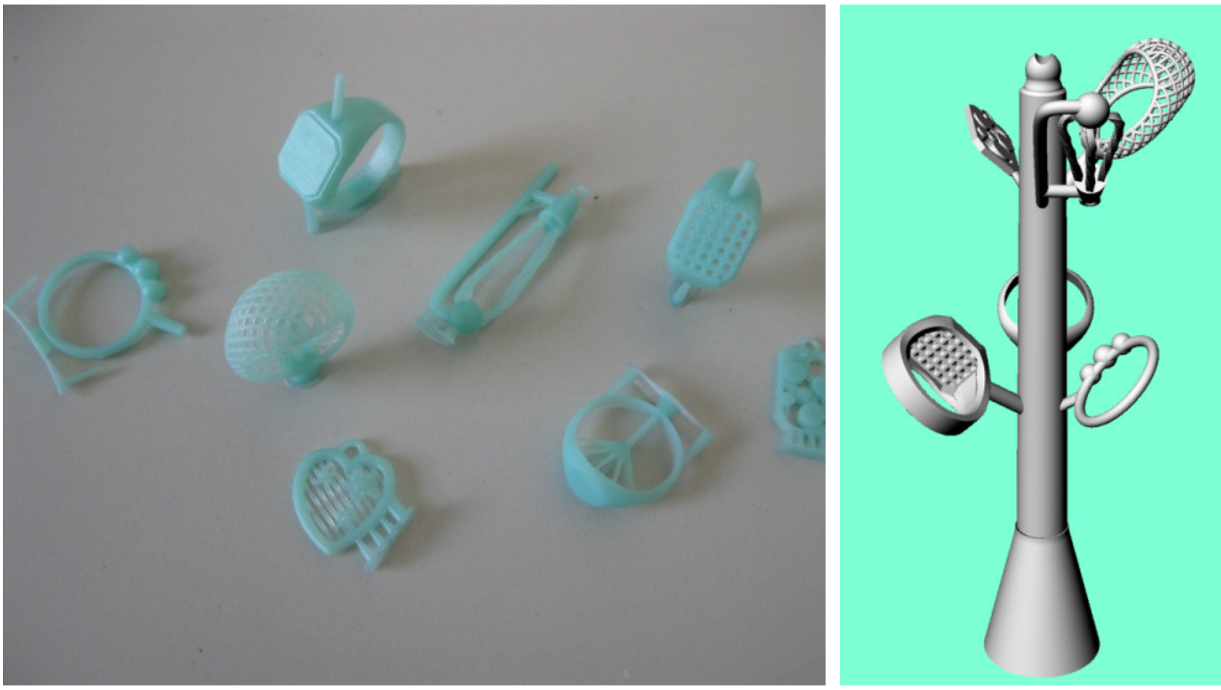
The table below shows the area/volume index characteristics of some of the above items.

Tab 1 Object identification and Area/volume index for the main models used.



A/V index	3.45	2.05	1.76	1.64	1.59	1.48
ID	Cage ring	Dog-tag	Dropper	Sphere ring	Oval signet	Rectangular signet

The standard casting tree comprised the six items shown in table 1 above with the thin models (high A/V ratio) positioned in the upper part and the solid items (low A/V ratio) in the lower part.



a)

b)

Fig. 11 Example of resin used to evaluate castability (a) and standard tree configuration (b)

The casting simulation activities carried out beforehand provided the know-how to optimise the casting system and the process parameters (in terms of mould and metal temperature) [12,13].

Casting was performed using static casting ovens with a vacuum-pressure system. The trees were made of silver 925 with mould and casting temperatures of 500°C and 985°C respectively.
Different parameters were taken into consideration thoughout the entire project, such as resin conditions, the characteristics of the coating, calcination cycles, etc.
100x150 mm flasks were prepared using a vacuum-packed mixer to prepare the coating.
Two different coating powders were used: a specific coating for resin casting designed specifically to give high expansion and strong resistance (coating A) and a general coating (coating B). The materials were tested at different water/powder ratios: 36:100, 38:100 and 40:100. Different calcination conditions were analysed and compared with the thermal analysis conducted on the resins.

Cycle 0: consisted of three different steps at 150°C, 400°C and 750°C, reached with an average speed of about 1.9 °C/min and maintained for 4 hours. The flasks were then cooled to room temperature and turned upside-down two hours before casting.

Cycle 1: consisted of three different steps at 150°C, 270°C and 730°C, with an average speed of 1.75 °C/min and maintained for 4 hours.

Cycle 2: the longest cycle, consisted of four different steps at 150°C, 315°C, 480°C and 730°C, with an average speed of 1.1 °C/min and maintained for 4 hours.

Cycle 3: a fast cycle that involved the flasks being placed directly in the oven at 600°C. After 40 minutes, the oven temperature was raised to 730°C. In this case the average heating speed was 18.25°C/min.

The following graphs summarise the various calcination cycles.

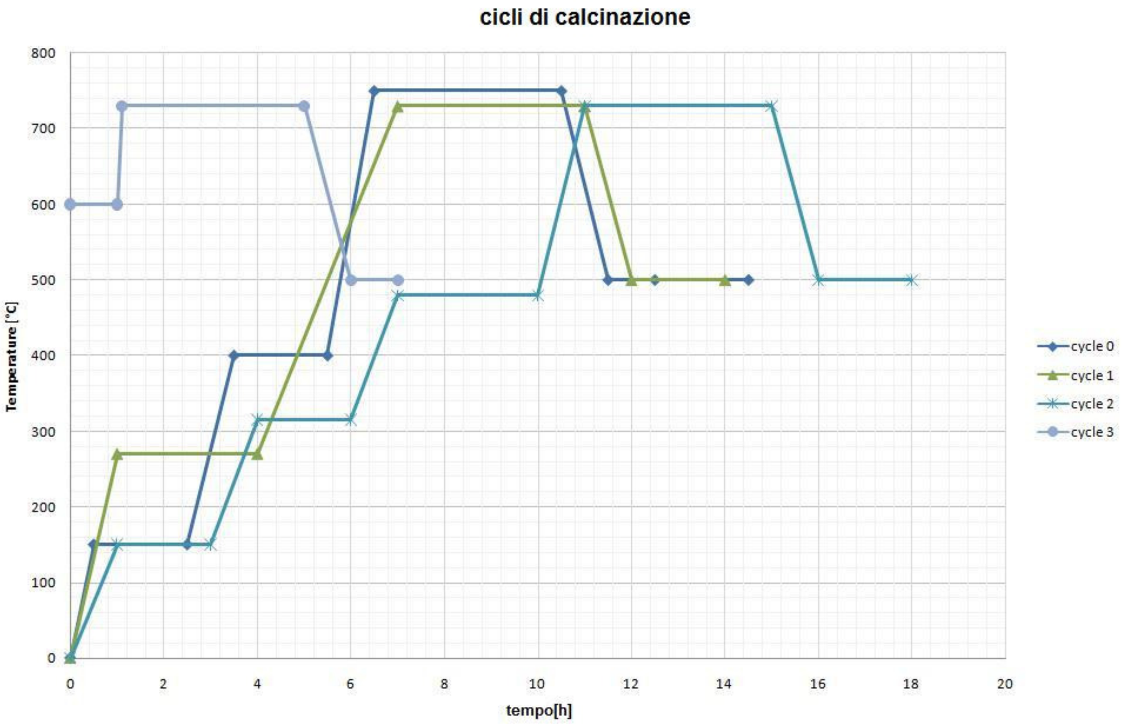


Fig. 12 Graph regarding the calcination cycles analysed

Both static and fan ovens were used in order to assess any possible influence on the final quality of the parts.

Other resin characteristics such as lifetime, degree of UV reticulation and the effect of surface cleaning were also taken into consideration.

Polymeric materials tend to age. In other words, their properties tend to change over a period of time. These changes can depend on various factors, for example, a chemical reaction, as in the case of the progressive reticulation of a thermo-hardening material, or interaction with the environment, as in the case of oxidation and thermo-oxidation [14,15].
The use of resin samples with modified properties can lead to unexpected results. Casting tests were therefore carried out on super-reticulated or thermo-oxidised components in order to observe the quality of the final objects.

The various casted parts were then analysed in terms of surface, using an LEICA ME5 stereo-microscope with 6.3X magnifying power.

Calcination cycle analysis

Under real calcination conditions and actual interaction between resin and coating, some practical analyses were made to gain a deeper knowledge of the process.
Heat transfer through the coating both during the calcination cycle and the casting process was extremely important, as previous studies have confirmed [16,17].
An experimental test was therefore carried out by introducing a test flask into the oven equipped with thermocouples in order to map the oven and obtain information on the cycle that the coating material was actually undergoing.
The temperature sensors were placed in such a way as to acquire information relating to the various positions of the tree both in terms of level and radial distance from the main shaft.

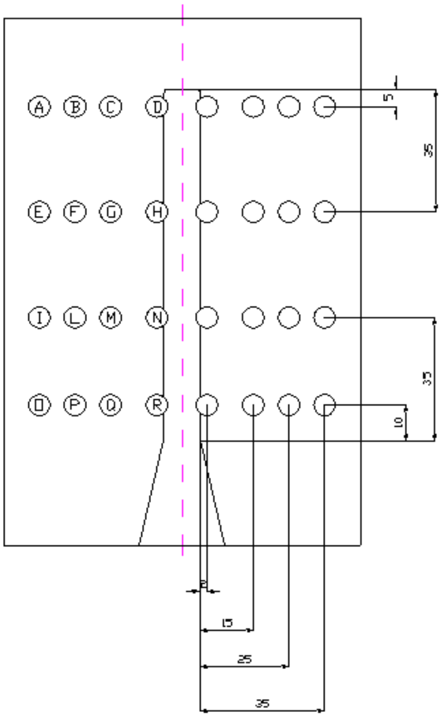
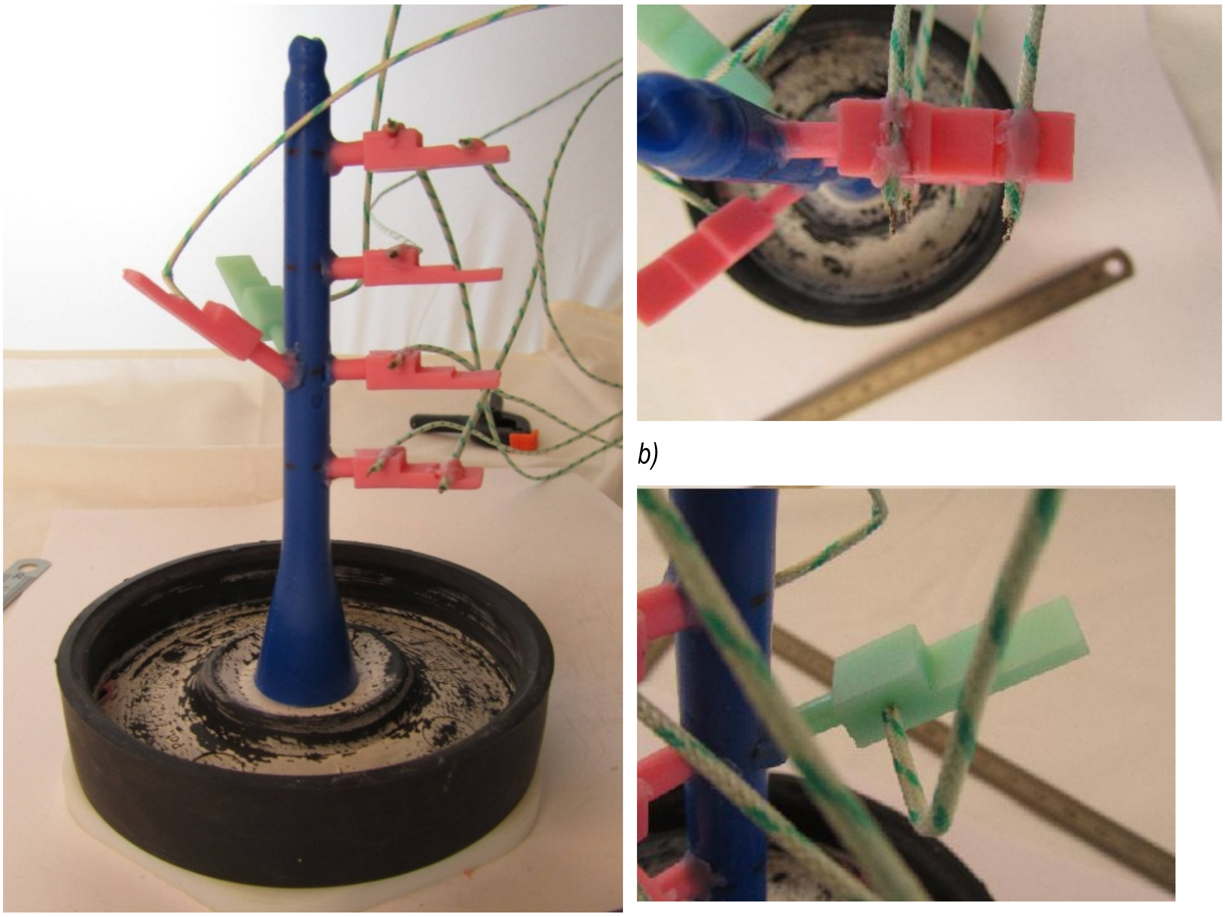


Fig. 13 Positioning of the thermocouples inside the flask. All the sensors were placed 4 mm inside the coating.

The first set of tests was conducted on a standard tree with 4 different levels and 4 different radial distances from the central shaft so as to obtain information on the temperature at different times and in various positions. Measurement tests were also performed by comparing the internal temperatures of a piece of wax with a corresponding piece of resin.



b)

a)

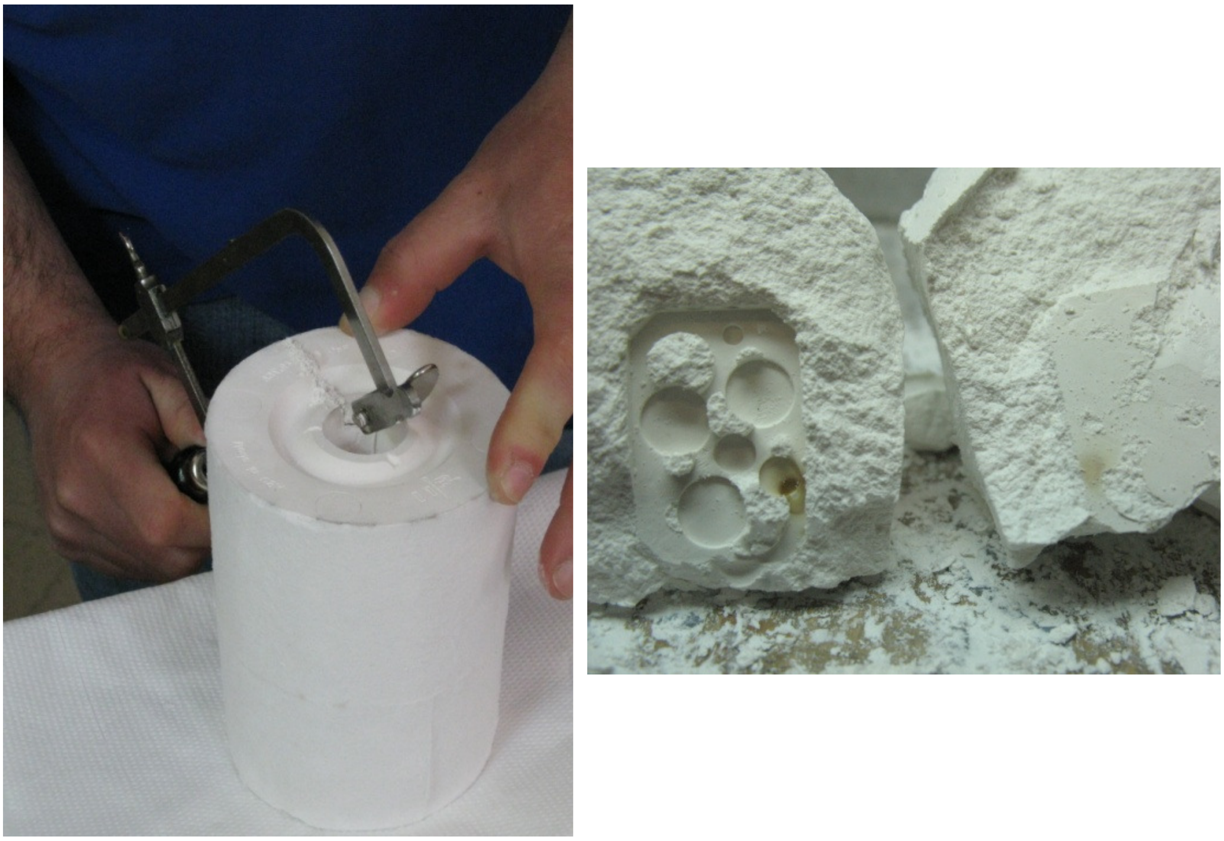
c)

Fig. 14 Sample tree with thermocouples in the coating (a) (b) and in the resin (c).

The temperature was measured every 20 seconds both during the baking cycle and during the subsequent cooling in the air.

This information proved to be precious in understanding the behaviour of the coating and in obtaining information on the true thermal stress on the material during the various calcination cycles.

Another important step is to understand the common interaction phenomena that occur between the resin and the coating. For this reason an experimental type-test was carried out. After the calcination cycle, some flasks were allowed to cool and were then cut in order to let the light into the cavities left by the wax and resin models. These cavities were then analysed under a SEM scanning electron microscope with EDS microprobe analysis.



a) *b)*

Fig. 15 Opening the coating after calcination (a). An example of a cavity (b).

In some cases, this analysis led to the observation of a layer of coating that had been strongly affected by chemical reactions, a sure sign of a degradation mechanism.
The thickness of this layer, depending on the specific conditions, measured up to 150µm.

Results

Analysis of the surface quality of the resins

The research examined various rapid prototyping resins each created using different commercial technologies. These were analysed, used for casting and observed in terms of the quality of the final piece.
With the various technologies available, identical models were created using constructive parameters that would allow for the components to be appropriately compared.
In particular, the objects were obtained trying to maintain the best compromise between dimensional precision and creation speed. For the sake of brevity, this paper only reports the examples that are more indicative of the various problems/opportunities linked to the use of direct casting resin.
It was firstly necessary to perform an assessment of the surface quality of the prototyped piece paying particular attention to the evenness of the surface, the accuracy of the reproduction and any defects.
The photographs below show the results in terms of surface quality of some types of resin and aim at highlighting how, different shapes and construction techniques can lead to different surfaces that obviously affect the quality of the finished piece.

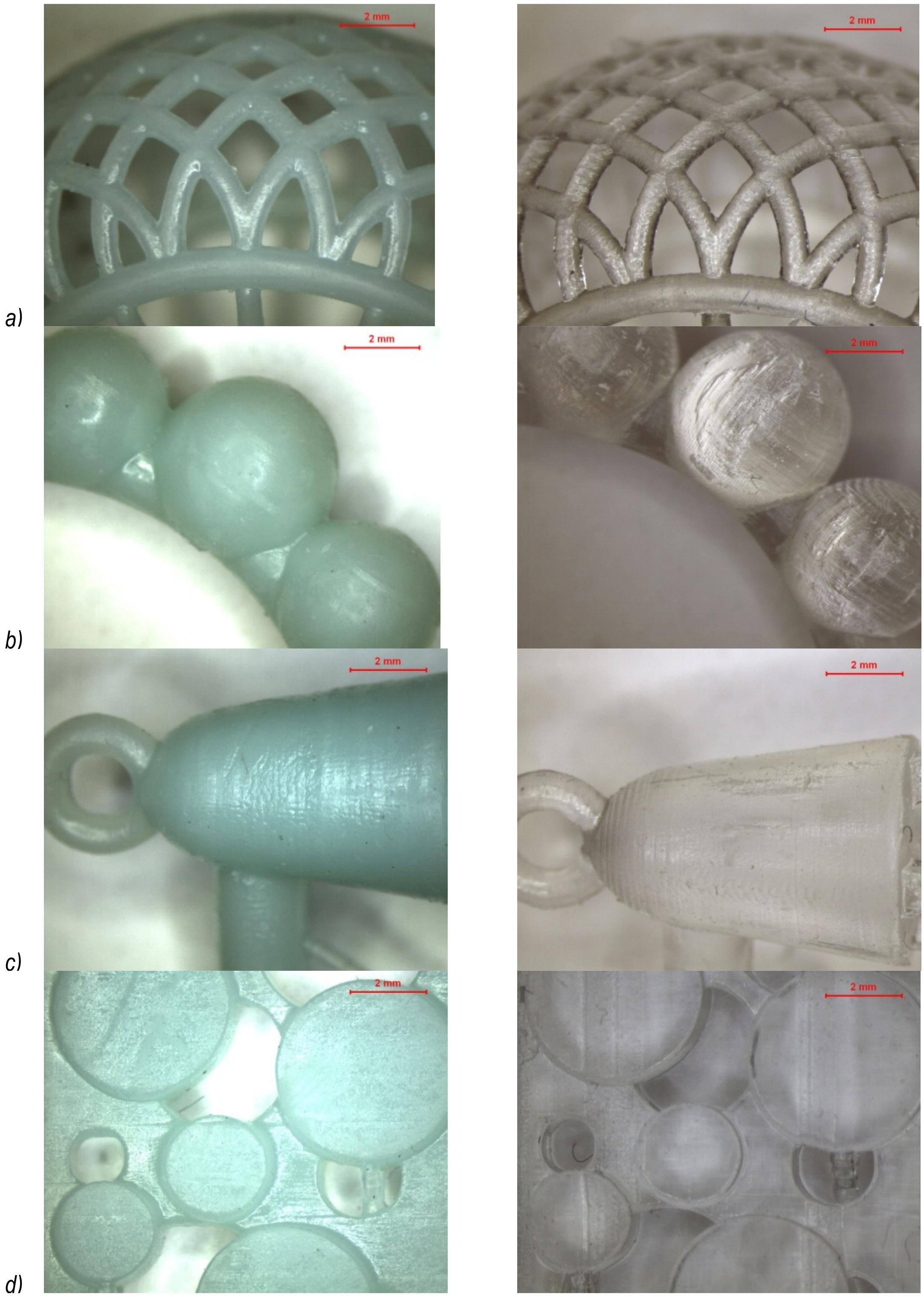
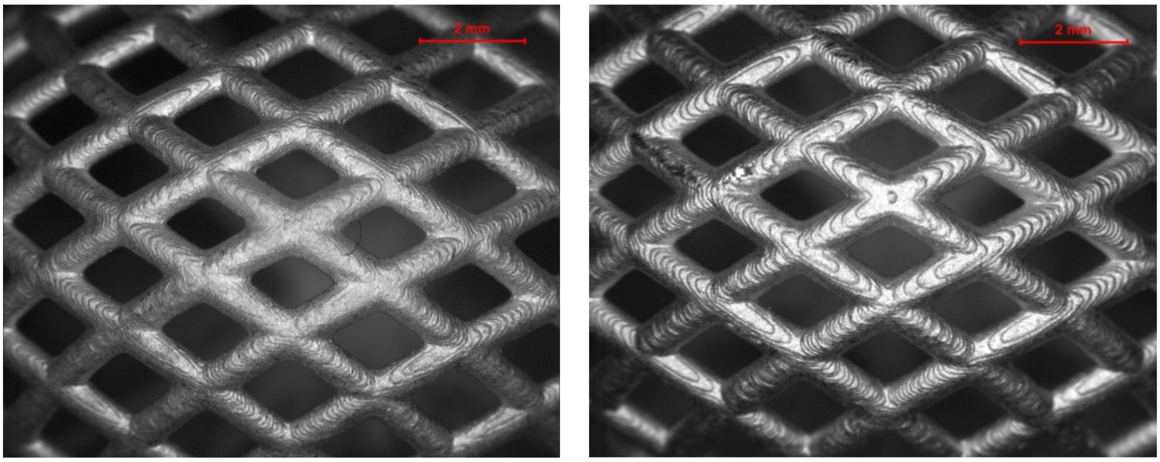


Fig. 16 surface detail of various commercial resins used to make filigreed items (a) and curved (b) and (c) or flat (d) surfaces.

When observing the quality of the casted piece, the origin of the surface characteristics should be assessed by distinguishing which are ascribable to the process and which arise from the original properties of the model.
In fact, it should be remembered that different materials and processes can produce objects with different characteristics.

The example in figure 17 illustrates how different materials respond differently to the creation process and produce various degrees of slicing marks.



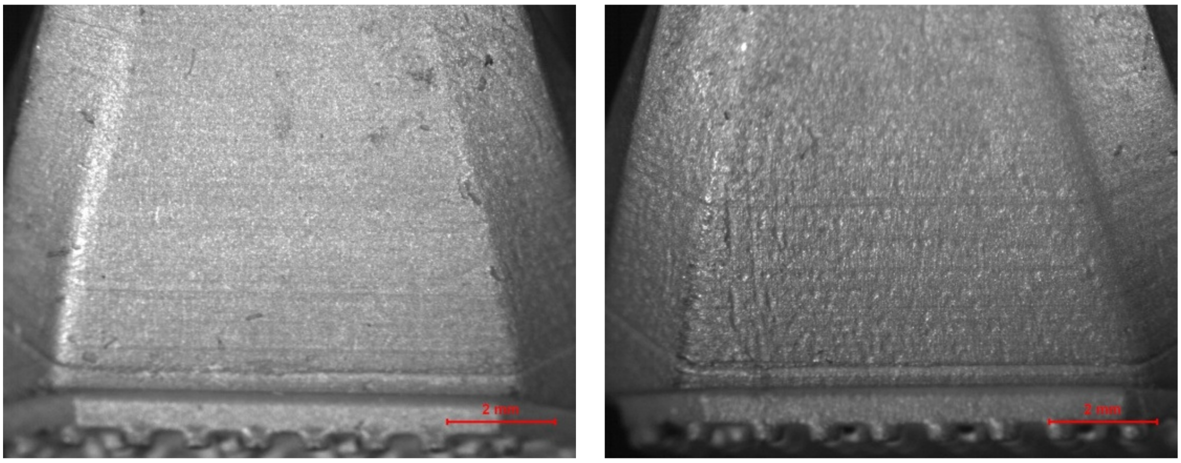
a) b)

Fig. 17 Surface detail of casted parts using different kinds of resin.

Characteristics deriving from the conditions in which resins are used

It is known that the aspects of the final object strictly depend on the characteristics of the resin from which the item was obtained. In particular, the preservation and treatment conditions of the resin object can significantly affect the final quality of the casted item. Some of the factors linked to the preliminary treatment of the prototyped object, are the removal of the construction supports, the time between producing the object and its use and the surface cleaning of the resin itself.

For some types of resin, producers recommend paying particular attention to cleaning the models before assembling the tree. For some materials being in a hot environment can cause the formation of an oily sheen on the sample surface. It is advisable to wash the sample in alcohol and dry it well in order to avoid this problem. Figure 18 below highlights the effects of washing. It can be seen how this treatment gives a smoother surface and, at the same time, removes the oily sheen which can have negative interaction effects with the coating during the calcination phase leaving the final object with a dotted surface.

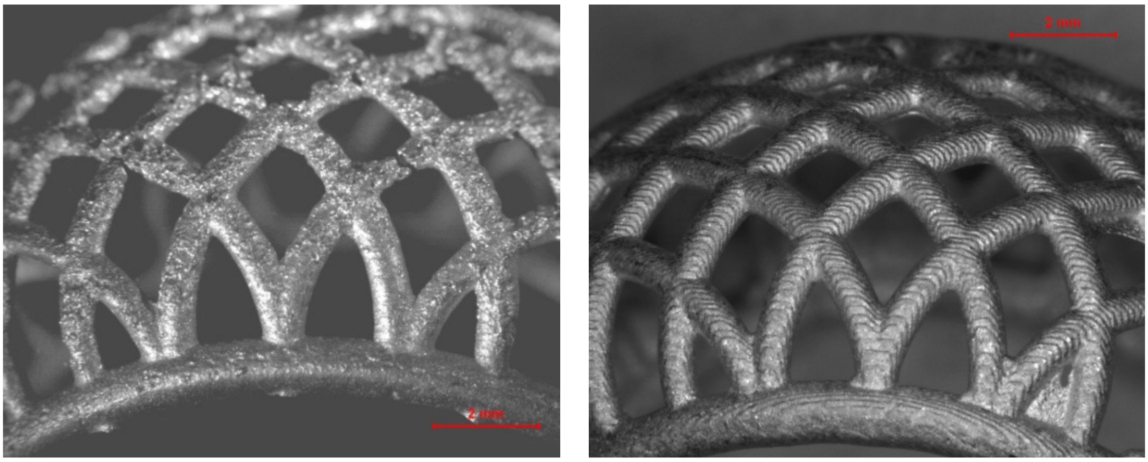


a) b)

Fig. 18 Surface detail of casted parts on which surface cleaning has been carried out (a) and has not been carried out (b).

Particular attention must also be paid when the supports are being removed and during resin filling. Filling is traditionally one of the critical points in the micro-fusion process in consideration of its fundamental role during the wax elimination phase and when casting molten metal. Its function is even more important in the case of the

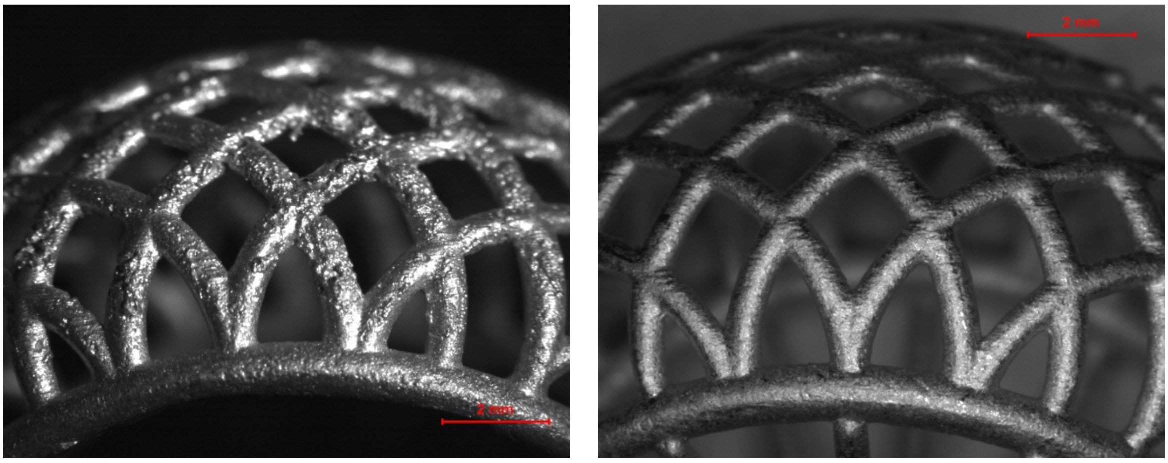
direct casing of rapid prototyping resins. Filling the geometric shapes of the items concerned in the project was optimised by casting simulation. Despite this, some shapes demonstrated the need for further filling to improve the resin disposal phase.
Figure 19 below compares the same filling system for a resin model (a) and a wax model (b), showing how this filling system works, in terms of thermo-fluid dynamics.



a) *b)*

Fig. 19 surface detail of the casting of a cage ring: resin model (a) and wax model (b).

It is obvious how the same filling system works in different ways in both these cases. Another filling channel was provided for the resin component, maintaining the supports inside the ring. The figure below shows the results.



a) *b)*

Fig. 20 Surface detail of the cage ring component removing (a) or maintaining (b) the original internal supports.

As previously shown, maintaining the supports improves filling but it is also obvious how this is the only solution for obtaining a quality finish.

Lastly, particular attention must be paid to preserving the resin items. It is normally advisable to use resin components within 4 – 6 weeks of production, coating them with appropriate acrylic-based sprays and keeping them away from the light in containers dehumidified with silica-gel. These indications are not often followed in industrial practice and resins that have been kept for longer periods of time, and which are therefore old, are often used.
Polymeric materials are sensitive to the environmental conditions to which they are exposed, both in terms of air and light[18].

The two conditions are normally present when objects are not preserved correctly or their production has taken too long. The photographs below show how “new” objects have better surface characteristics than “old” ones.

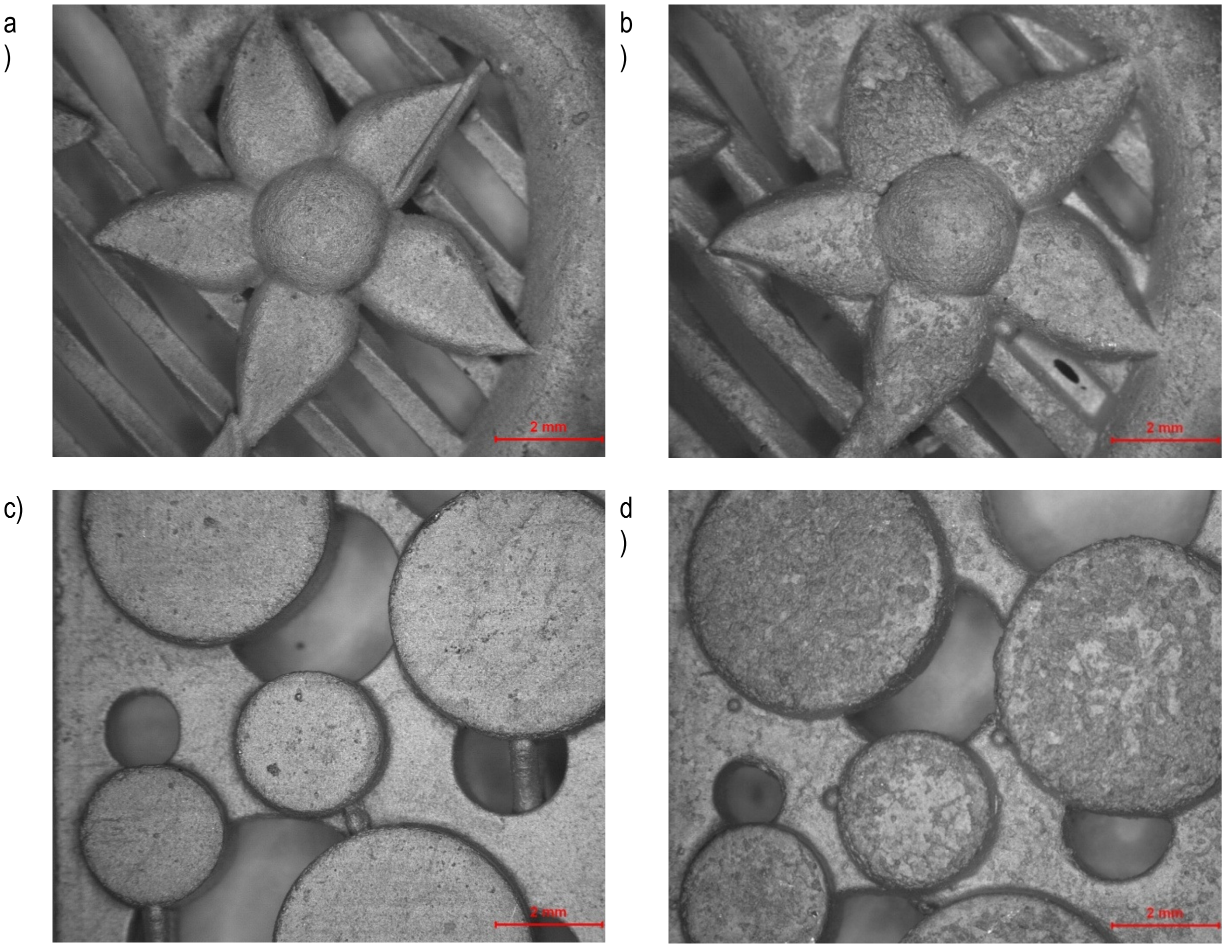


Fig. 21 details of the surface quality of different objects obtained with optimal parameters under standard conditions (a), (c) and after aging (b), (d).

In order to analyse the effect of the various phenomena, experimental tests were prepared to reproduce the natural aging conditions and to analyse the effects separately.
Firstly, to evaluate the effect of overexposure to UV rays, the various materials were exposed to aging cycles with UV for 15 and 30 minutes or so, and were then used to make “optimal” trees.
At the same time, an accelerated thermo-oxidising aging was conducted on some samples for 24 and 72 hours.

The following photographs show how the two artificial aging processes affected the quality of the final product.

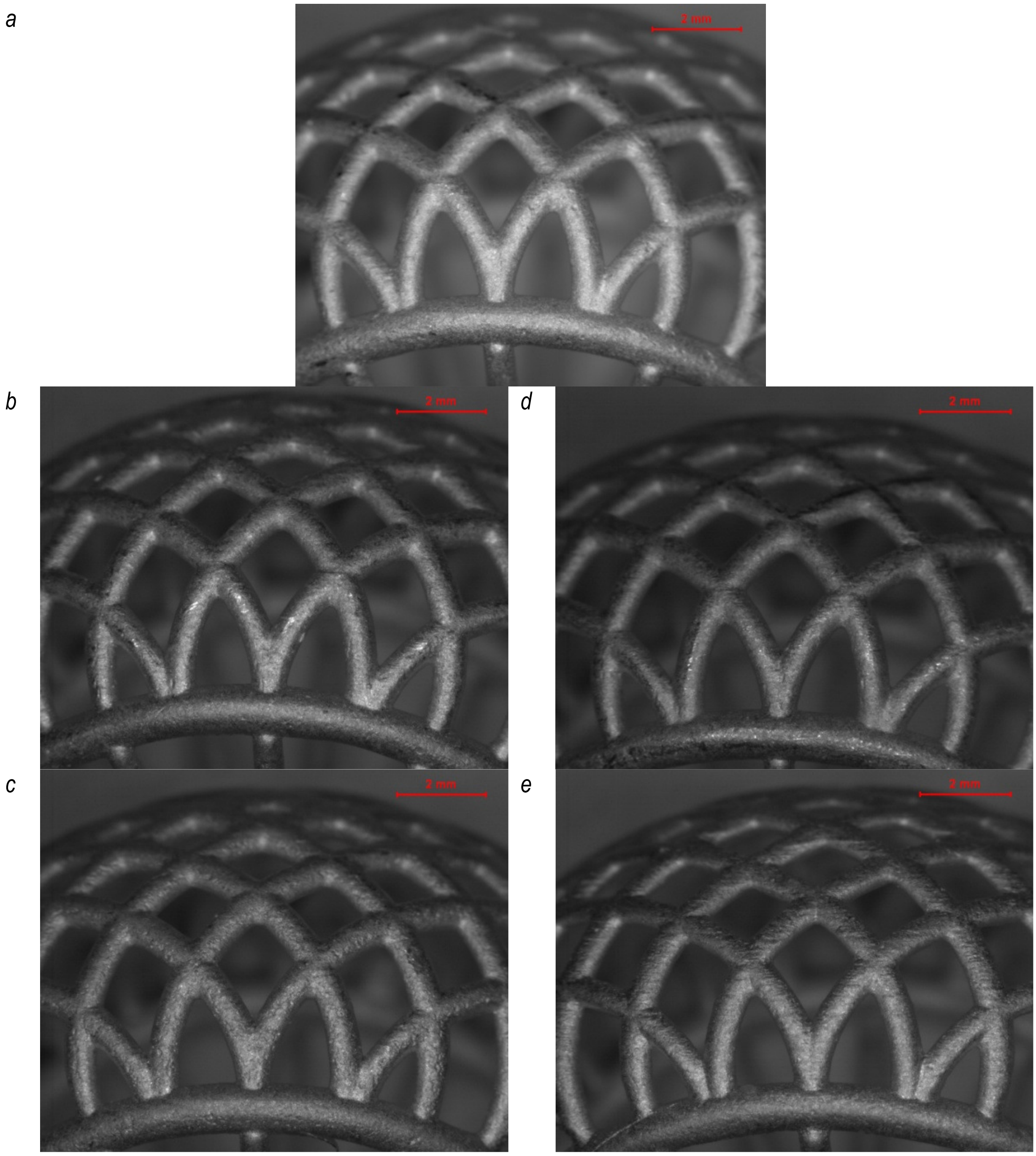


Fig. 22 detail of the surface quality of a cage ring obtained with optimal parameters under standard conditions (a), after UV aging for 15 minutes (b) and 30 minutes (c) and after thermo-oxidised aging for 24 hours (d) and 72 hours (e).

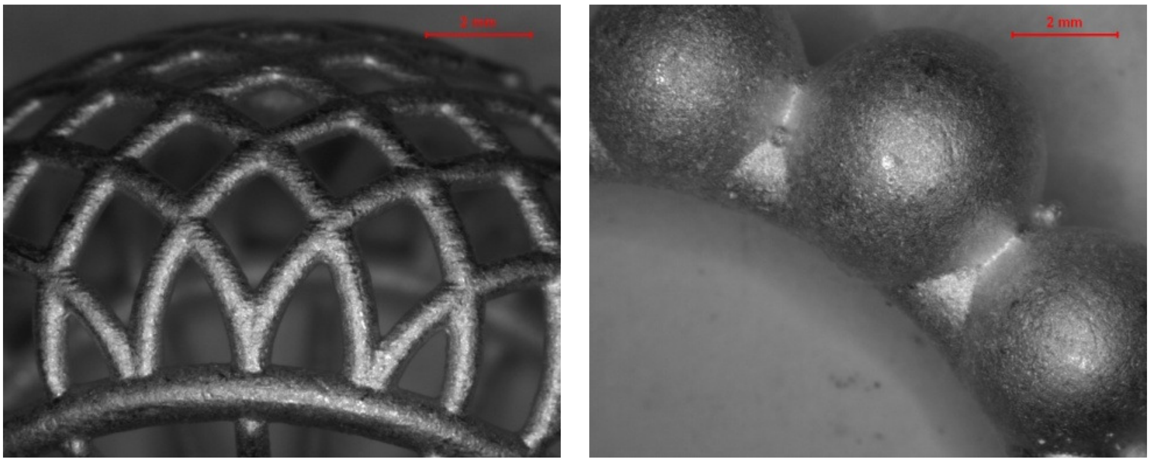
Surface deterioration can clearly be seen in the aged samples both after UV ray exposure and exposure to a thermo-oxidising atmosphere.

Coating and water/powder ration

Several coating powders are available on the market both for general use and for specifically studied resin uses. By testing various powders under the same conditions, it is possible to understand how different process parameters can affect the various materials.

The photographs below shown the results of casting under "optimal" conditions (in terms of baking cycle and water/powder ratio) both for specific coating for casting resin (coating A) and for materials for general use (coating B).

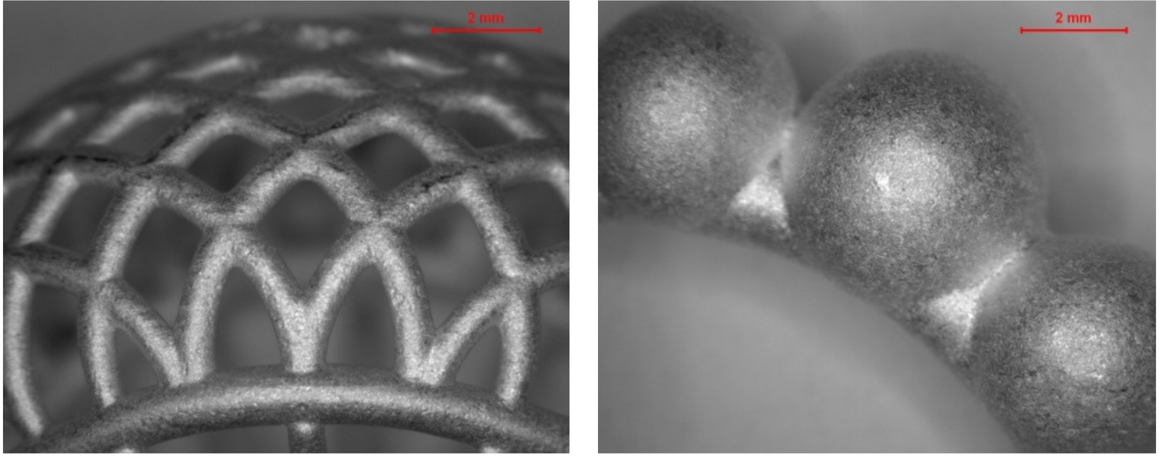
Figure 23 shows the casting results using a specific coating for both thin and thick objects. The use of this type of coating with a water/powder ration of 38:100 gives good results on both types for object.



a) b)

Fig. 23 surface quality of casted objects using a specific coating for resin with a water/powder ration of 38:100. Cage ring (a) and sphere ring (b).

Figure 24 below shows the surface quality of a final piece obtained using a general coating product (material B). In this case too, an optimal procedure gives a quality finish.



a) b)

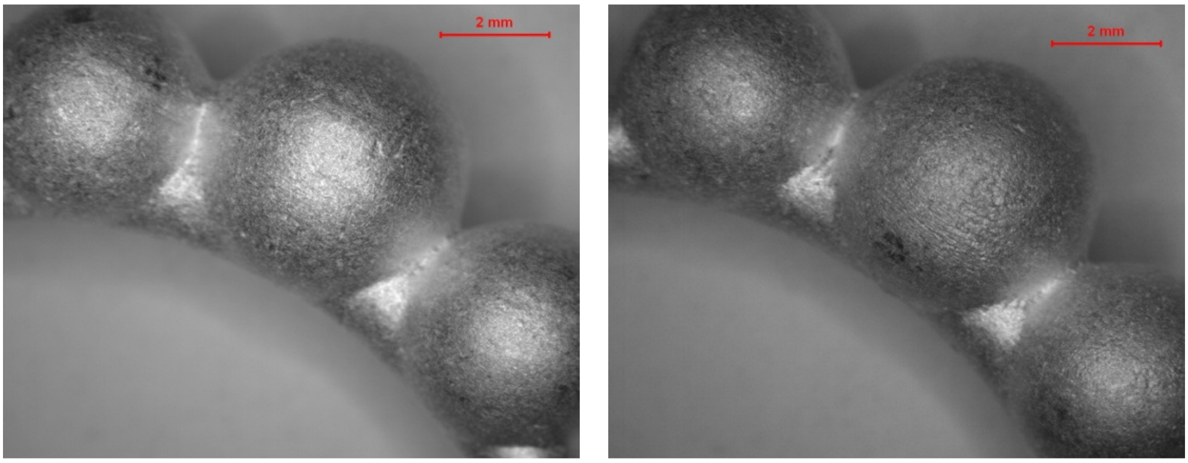
Fig. 24 Surface quality of objects casted with a general coating product with a water/powder ration of 36:100. Cage ring (a) and sphere ring (b).

Although there are no obvious differences in the final result, it is important to bear in mind that: the non-specific material is more severe in terms of process parameters, especially in reference to the water/powder ratio.

This parameter is traditionally very important in the micro-fusion process[19,20] and is fundamental when using rapid prototyping resins.

Therefore various casting tests were carried out using flasks with different water/powder ratios and considering the values included in the interval between those recommended for light objects and those recommended for thicker pieces.

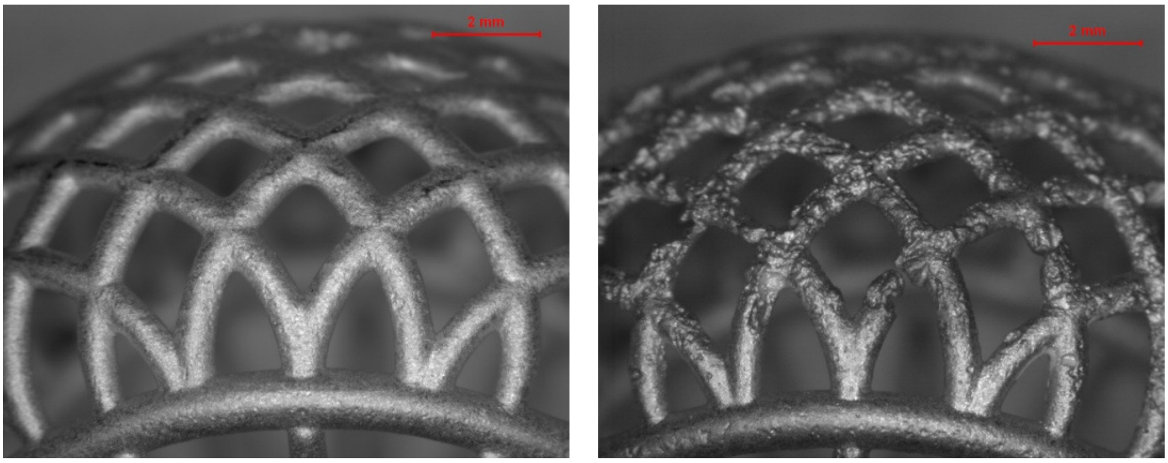
Figure 25 below shows a comparison between casting results using water/powder ratios of 36:100 and 40:100 using a general coating product. With medium-sized objects, it can be seen how an increase in water when preparing the coating gives a rougher surface.



a) b)

Fig. 25 Surface quality of a sphere ring using a general coating with water/powder ratio of 36:100(a) and 40:100 (b).

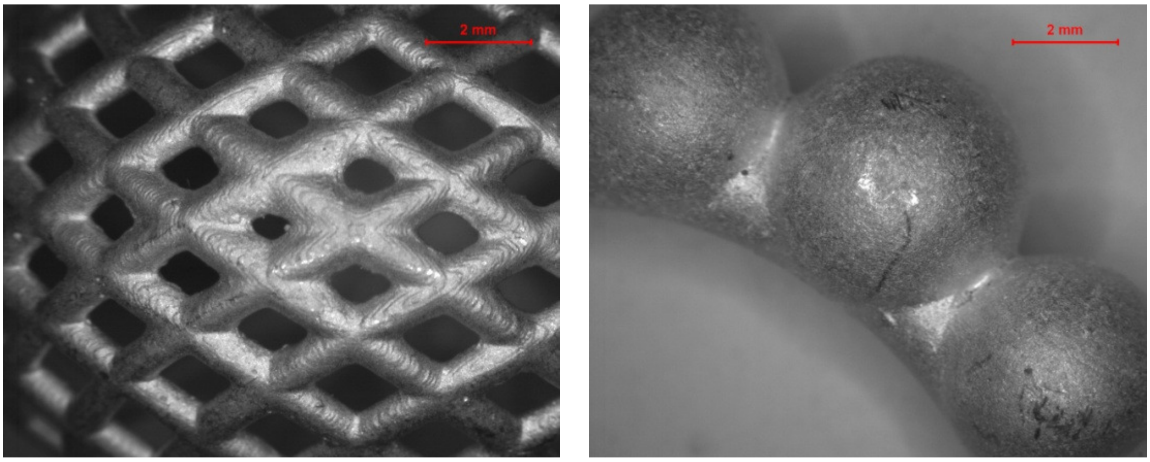
This phenomenon is further highlighted with fine objects. The cage ring shown in figure 26 below is a particularly difficult piece due to the high level of specific surface (high Area/Volume index). Fine objects are therefore more sensitive to the interactions between resins and the surface coating.



a) b)

Fig. 26 Surface quality of a cage ring using a general coating with a water/powder ratio of 36:100 (a) and 40:100 (b).

The effect of this variation in water/powder ratio was analysed for both general (B) and specific (A) coatings. The following photographs show the effect of a higher water/powder ratio of 40:100 for specific coating (A).



a) b)

Fig. 27 Surface detail for cage ring (a) and sphere ring (b) obtained with specific coating at 40:100

In this case the surface quality of a casted piece was less affected by the high water/powder ratio. This effect strictly depends on the characteristics of the coating material and the resin.

Calcination cycle effect

Calcination cycles play a very important role in the micro-fusion process[21], firstly to eliminate the water content in the coating and then to try to eliminate any ash that forms as a result of resin decomposition.
The cycles can be classified on the basis of their duration defined as fast (less than 7 hours), rapid (about 11 hours) and slow (more than 16 hours) [22].

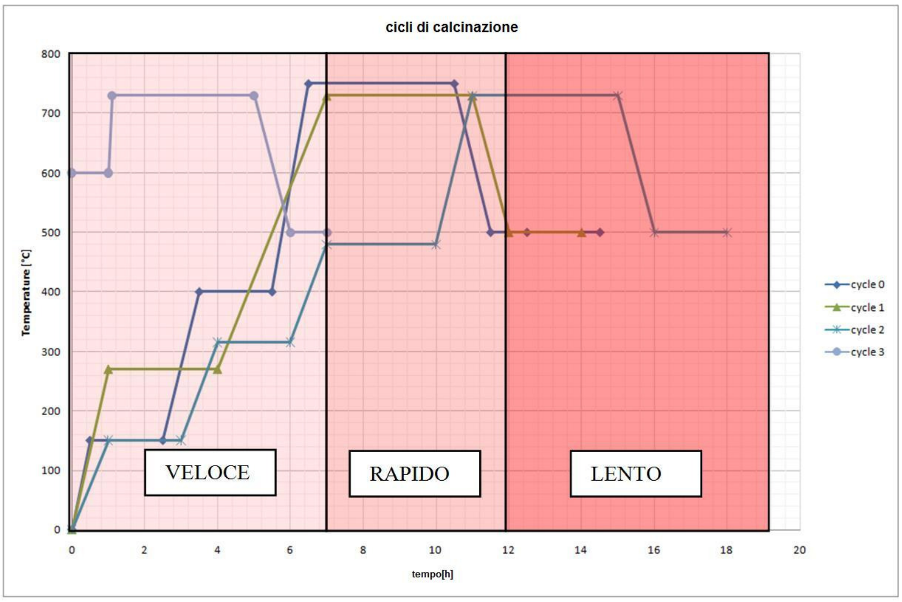
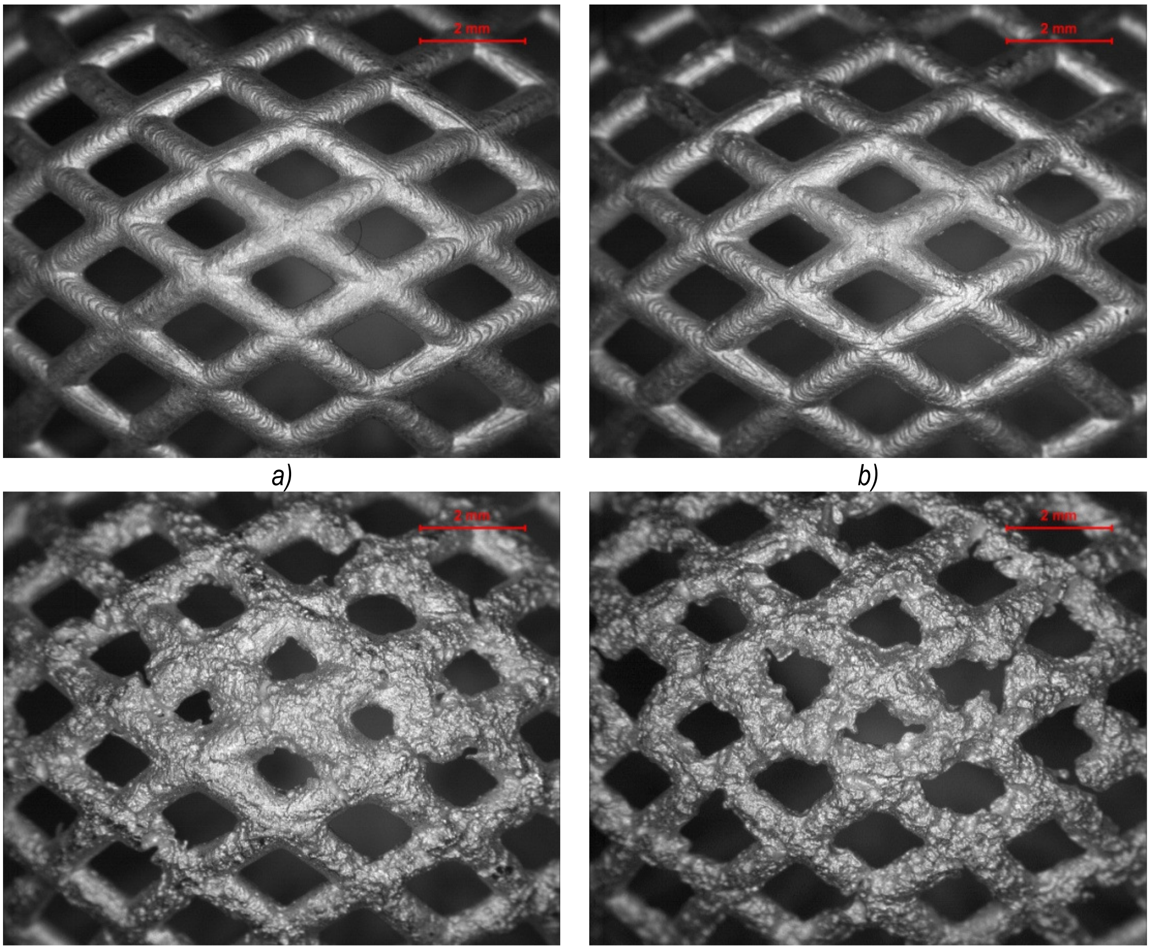


Fig. 28 Classification of the calcination cycles examined.

The choice of calcination cycle must bear in mind the type of components that the tree to be obtained is made up of, finding the right balance between heavy and light parts. Figure 29 below shows the effect of different cycles on a fine object.



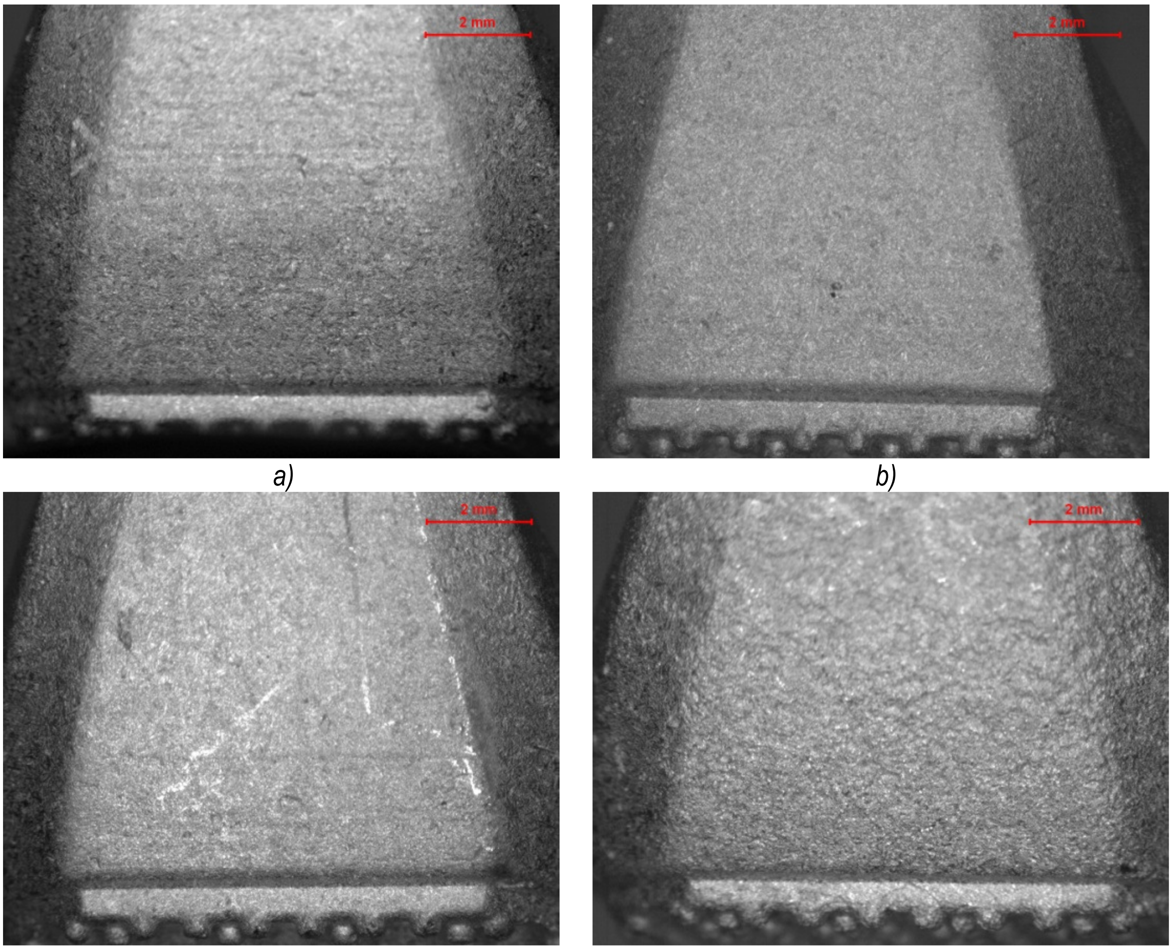
a) b)

c) d)

Fig. 29 Surface quality for a cage ring obtained with cycle 0 (a), cycle 3 (b), cycle1 (c) and cycle 2 (d) with coating A at 38:100.

The surface quality diminishes for the longer cycles: cycle 2 is the one that gives the worst results. A comparison between cycle 0 and cycle 3, which underwent the same average heating speed, shows considerable differences, probably due to the rotation of the flask at the end of cycle 0 which gives a better change of air in the oven chamber.

A similar approach was used to identify the best cycle for heavy and thick parts.

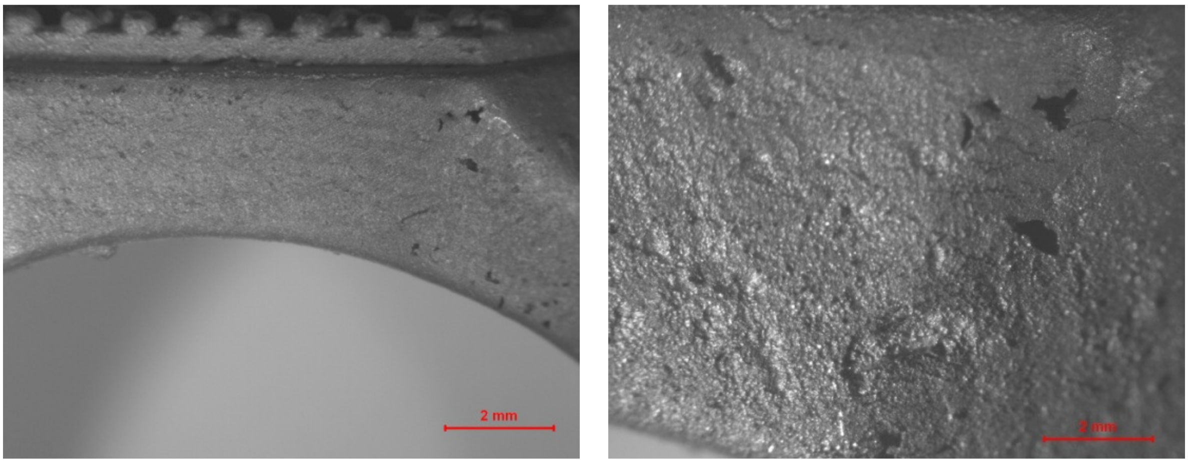


a) *b)*

c) *d)*

Fig. 30 Surface quality for a signet ring obtained with cycle 0 (a), cycle 3 (b), cycle1 (c) and cycle 2 (d) with coating A at 38:100.

Optimal results can be achieved for “heavy” pieces in terms of surface quality by using rapid or fast cycles. A more detailed analysis of fast cycle results shows the presence of surface cracks caused by the thermal stress to which the coating is subject.



a) *b)*

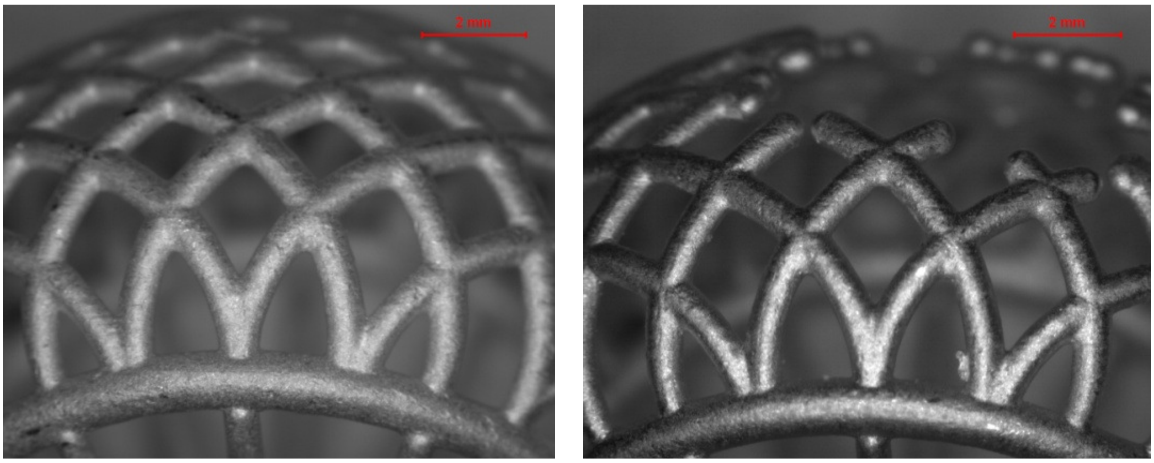
Fig. 31 Detail of the surface cracks on solid objects obtained with a fast cycle (cycle 3).

The best compromise is therefore the use of rapid cycles, especially cycle 0.

Characteristics of the calcination oven

The use of a calcination oven equipped with air circulation devices inside the chamber alters the results in terms of the quality of the finished product. This is normal in reference to the traditional micro-fusion process but is a key factor in the specific case of direct resin casting.

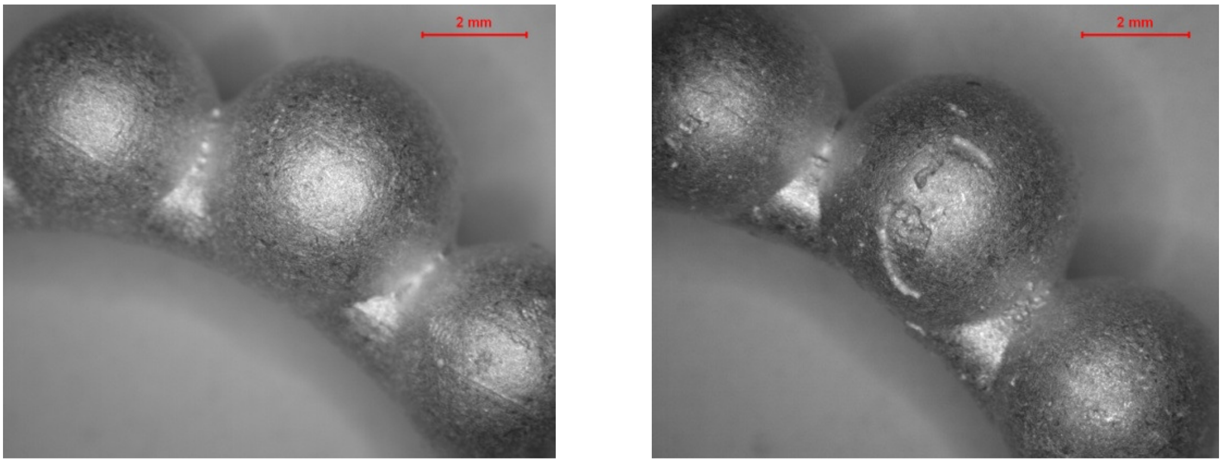
The affect this factor has was analysed during the process by performing a calcination cycle using both traditional static ovens and fan ovens.
The following photographs show how this choice can affect the final quality of the product.



a) b)

Fig. 32 Surface quality detail of cage rings obtained with optimal parameters in a fan oven (a) and a static oven (b).

The poor surface quality of the fine objects is rather evident. This problem can appear in different ways: the presence of residue can obstruct the flow of metal inside the cavities or there may be a chemical interaction on the surface which causes a reduction in quality.



a) b)

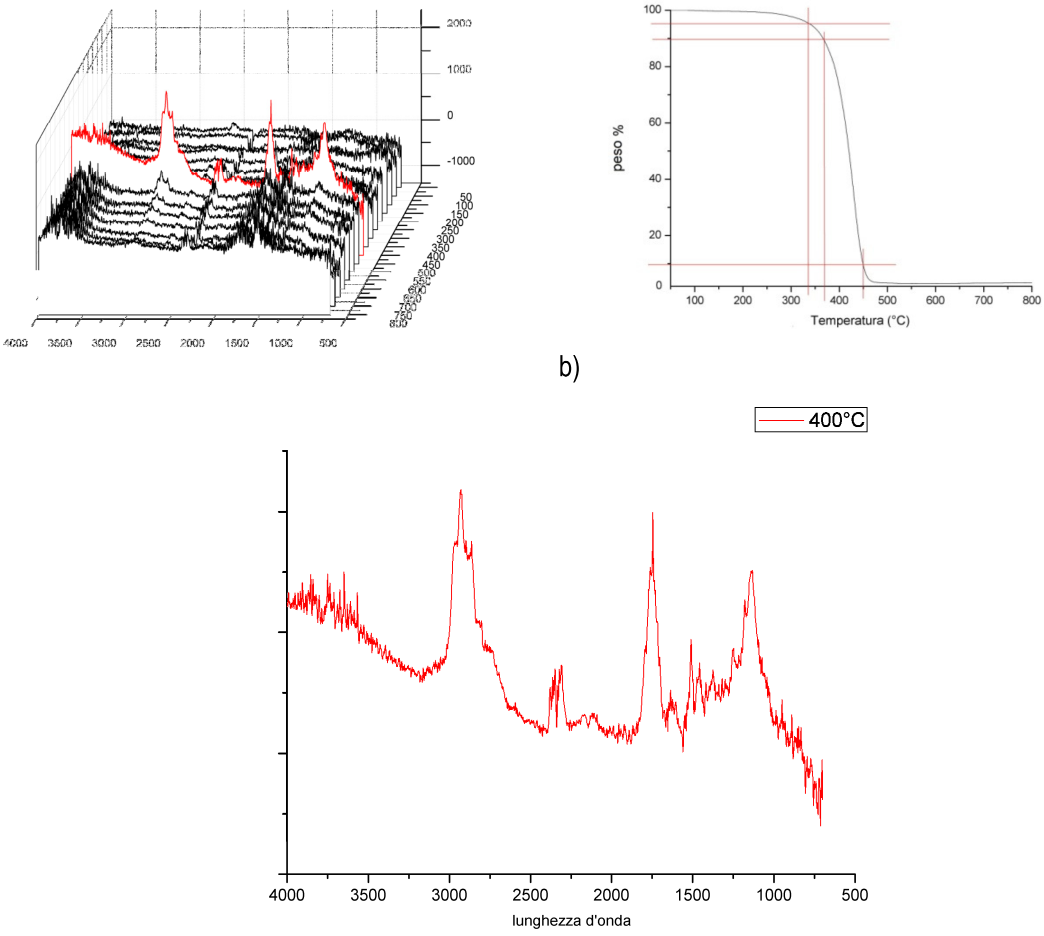
Fig. 33 Surface quality detail of sphere rings obtained with optimal parameters in a fan oven (a) and a static oven (b).

Using a static oven the surfaces of medium-heavy components are coarse and rough. The advantage of using a fan oven can easily be observed both in terms of surface quality and the porosity of the casted items deriving from carbon and gas residue during decomposition.

One possible interpretation of the combined effect of optimal calcination cycles and the use of fan ovens can again be demonstrated by laboratory analysis.

By using TGA-IR analyses, a sampling of gas deriving from the decomposition of the material can be coupled to thermo-gravimetric analysis.

The graphs below show the TGA curve associated to the relative analysis spectrums and the detail of the analysis spectrum in correspondence to the maximum decomposition speed.



a)

b)

c)

Fig. 34 TGA curve (a) associated to the relative analysis spectrums (b) and detail of the analysis spectrum corresponding to maximum decomposition speed at 400°C (c).

On observing these graphs, it can be seen that, in correspondence to the maximum decomposition temperature, different types of formations occur and CO_2 is also present (2350 cm^{-1}).

This type of analysis gives useful information on understanding what happens during the resin decomposition process.

The analyses concerned were carried out under controlled and oxygen-rich atmospheric conditions in which no interaction with the coating material was made and the tests were conducted in micro-scale.

Normally, when hydrocarbons (like waxes and resins) are made to degrade, the reaction evolution depends highly on the oxygen content in the atmosphere. If the atmosphere has a poor oxygen level, pyrolysis occurs with the formation of CO instead of CO_2, which is lighter than air and therefore tends to get trapped in the cavities if the flask is placed with the opening downwards, in the traditional position for emptying wax.

Furthermore, the pyrolysis phenomenon causes the formation of carbon residue which, being trapped in the cavities, speeds up the coating decomposition process.

Conclusions

The rapid prototyping sector provides many technologies and materials that can be applied to the gold and jewellery industry. However, in order to achieve a complete and effective result with this method, it is necessary to have a good knowledge of the materials in order to find the correct approach for using rapid prototyping for the direct casting of models.

The key point for determining a procedure that guarantees a top quality product is understanding the thermal and physical properties of polymeric materials. The casting process involves many parameters. Only a combination of appropriate resins and optimal process conditions can determine the excellent quality of the finished products.

It should, however, be underlined that merely using "better" resins is no guarantee of getting a good final result. As an initial consideration it must be said that the use of "new" resins is the key to final quality. It is extremely important to prevent any kind of UV aging or oxidation of the material that may result from incorrect conditions or storage times. Moreover, the filling system must also be optimal to meet the specific needs of resins. Additional channels improve air circulation in the mould cavities and make it easier to remove residues.

The preparation and baking of the coating is also fundamental and particular attention should be paid to the water/powder ratio.

One of the most important phases is, however, flask baking, not only in terms of cycle but also with regard to the oven structure. Calcination, in fact, is a fundamental element of the whole process. Firstly, water must be totally eliminated so that the resin cannot absorb it (it can deform the mould surface). Then the resins must undergo total combustion and residue must be eliminated. This can only be achieved by an accurate balance between the various steps in temperature, depending on the size and shape of the models on the tree.

It is also fundamental to remember that the various steps in the calcination cycle are calculated on a theoretical basis. The ovens are usually able to create all the different phases programmed, but the real performance depends on the efficiency of the oven itself. To this regard, a fan oven clearly gives the best results. The use of a fan oven has a definite positive effect on the surface quality of the final product.

In order to obtain quality products using rapid prototyping resins, the effectiveness of the various parameters must be checked without necessarily upsetting the process itself. The process can, however, be fine-tuned to satisfy the needs of the resins.

To conclude the research, below are some considerations linked to the analysis of possible causes of defects deriving from the direct casting of resins. In order to understand the mechanisms of defect generation, a comparison must be made between their characteristics and the characteristics of wax defects, as follows:

Behaviour of the resin in the flask calcination phase	**Behaviour of the wax in the flask calcination phase**
Delayed casting and combustion	Early casting and combustion
Greater viscosity	Less viscosity
High carbon residue	Low carbon residue

The calcination of a flask containing resin models necessarily implies greater contact between carbon residues and the coating, which consequently determines greater interaction (as well as chemical reaction) between the residues themselves and the ligand (usually plaster).

A possible interpretation of this interaction can be deduced both in the negative and positive aspects. The negative signs are usually caused by the presence of carbon residues that lay on the surface of the coating during the metal casting phase. The positive signs, however, are caused by the presence of carbon residues that generate craters on the coating surface before metal casting. In accordance with the studies in Literature, the presence of carbon residues affects the decomposition of the anhydrous CaSO4 ligand, by increasing it, thus making the whole system less resistant.

Part of the research activity was financed by the EU INTOGOLD project.

Acknowledgments

The authors would like to thank:

- The partners of the INTOGOLD project for their precious indications and operative suggestions
- Frank Cooper and the JIIC – BCU group for providing the geometrics on which the research was conducted
- DWS for supplying the resin samples.

Bibliography

1. Frank Cooper, “Optimal practice for the use of different Rapid Prototyping systems”, *Proceedings of the 2nd International conference on Jewellery* Production Technology, (JTF Vicenza / Italy), 2005, pg. 121
2. Gay Penfold, “Designing for Rapid Manufacturing and other Emerging Technologies”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2008,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2008).
3. Joseph Tunick Strauss, “Rapid Manufacturing and precious metals”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2009,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2009).
4. Gay Penfold, “Industrial liaison and training in the UK Jewellery industry ”, *The Santa Fe Symposium on Jewellery Manufacturing technology 2004*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2004).
5. Steve Adler and Teresa Fryé, “Getting up to speed: Original research into casting rapid prototype models”, *AJM magazine* (August 2005).
6. Steve Adler and Teresa Fryé, “The revolution of CAD/CAM in the casting of fine jewelry”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2005,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2005).
7. G. Penfold and F. Cooper, “Current Practices in the use of various rapid prototyping systems in the manufacture of Jewellery and Silversmithing, *Jewellery Technology Forum (JTF*2005)
8. Ian McKeer. “Improvements in the burnout of resin patterns”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2007,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2007).
9. K.D. Desai, “Innovative lost wax investment casting technique”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2005,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2005).
10. N.P. Cheremisinoff*, Polymer Characterization - Laboratory Techniques and Analysis, (* William Andrew Publishing 1996)
11. Allan H. Fawcett, *Polymer Spectroscopy*,(John Wiley & Sons 1996)
12. Marco Actis Grande, “Computer simulation of the investment casting process: Widening of the filling step”, *The Santa Fe Symposium on Jewellery Manufacturing technology 2007*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2007).
13. Jörg Fischer-Bühner, “Improvement of sterling silver investment casting”, *The Santa Fe Symposium on Jewellery Manufacturing technology 2006*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2006).
14. Plastics Design Library Staff , *Effect of Temperature and Other Factors on Plastics*, (William Andrew Publishing, 1990)
15. Audouin, L. et al., "Role of oxygen diffusion in polymer ageing: kinetic and mechanical aspects", Journal of Materials Science,
16. Shankar Aithal, Denis Busby and John C. McCloskey, "Evaluation of mold burnout by temperature measurement and weight loss techniques," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2002,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2002).

17. Anatoly Kolomeisky, “Physical-Chemical Analysis of the factors Influencing the Behavior of Flasks During the Heating in the jewelry casting process. Development of the optimal model of burnout furnace.”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2004,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2004).
18. Jim R. White**, “**Polymer ageing: physics, chemistry or engineering? Time to reflect”, Comptes Rendus Chimie,Volume 9, Issues 11-12, November-December 2006, Pages 1396-1408
19. Ralph Carter, “Does Investment Permeability Impact Jewelry Castings?”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2004,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2004).
20. Ralph Carter, “Effects of Changing the Water-to-Powder Ratio on Jewelry Investments”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2001,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2001).
21. G.M. Ingo et al, “Thermal stability and chemical physical features of gypsum-bonded investment with regard to burnout cycle”, *The Santa Fe Symposium on Jewellery Manufacturing technology 2005*, ed. Eddie Bell (Albuquerque: Met-Chem Research,2005).
22. Marco Actis Grande, “Quality excellence in the direct casting of RP resins: reality or fiction?”, *The Santa Fe Symposium on Jewelry Manufacturing Technology 2011,* ed. Eddie Bell (Albuquerque: Met-Chem Research, 2011).