# THE EFFECT OF ALUMINIUM GRANULOMETRY ON THE BEHAVIOUR OF FILLED EPOXY RESINS FOR RAPID TOOLING

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## Abstract

Aluminium filled epoxies moulds have been used in indirect rapid tooling. These moulds, which have a low cost processing, are very competitive, when applied in the manufacturing of low volume series.

The geometry and the size distribution of the aluminium particles affect significantly the powder packing density, the resin ratio, the thermal conductivity, the curing time, the homogeneity and the mechanical characteristics of the tool.

Using three high temperature epoxy resins it was possible to understand the resin behaviour in the presence of the aluminium filler and formulate filled resins with the best compromise of mechanical, thermal and processing performance.

## Introduction

Tools manufacturing based in high strength resins is a promising technique included in the wide range of Rapid Tooling technologies [1-4]. The present research is focused in the behaviour analysis of three aluminium filled high temperature amine-cured epoxy resins. Different aluminium granulometry mixtures were employed in order to evaluate how they affect the mechanical and thermal performances of the composite tools, and the mixture processing and casting [5, 6].

It is expected that the matrix system present a low viscosity and a good wetting activity. On the other hand, after the resin mixture with the metallic filler, low viscosity or metallic fillers with wide particle size distribution increase the tendency for particles segregation, producing heterogeneous mixtures [7]. This segregation process is explained by the Stockes law, that sets up that the free settling velocity of spherical particles varies proportionally to the particles square diameter and to the inverse proportion of the fluid viscosity [8].

## Materials and Experimental Data

The letters A, B and C indicates the three high temperature amine-cured epoxy systems employed. The respective characteristics are presented in the table 1. A and B systems were acquired unfilled. C system, which is commercially available in the filled state, at a higher price, is used for comparison proposes. The manufacturers indicate the A and B systems for laminating applications. These two systems, when filled with metallic particles can be used in fillings and casting.

A and C system formulations result from the combination of high functional resins with low viscosity bifunctional epoxides, used as reactive diluents. B system is based in a more conventional formulation, resulting from the reaction between bisphenol A and F with epichlorhydrin [9, 10]. It exhibits higher viscosity than the A system, affecting the mixture capacity with metallic fillers. TGDDM resin (A system), which is based on aromatic glycidyl amine, is used in high-performance composites, showing a high Tg value (200ºC), a good thermal stability and resistance to the moisture, due to the high cross-link density [11]. Besides allowing a wide pot life, good wetting and impregnation capacity, the good reactivity of the epoxides groups produces a minimal performance reduction at elevated temperatures, which is a very important property for injection tools.

The reduced viscosity of the A system is due to the low viscosity of the reactive diluent, employed in a higher mixture concentration.

Three aluminium powders classes were used as metallic fillers. The different geometries and size particles distributions are indicated in table 2.

The aluminium concentration "phr" means the aluminium parts by weight per 100 resin parts. The aluminium content was kept at 250 phr for batches with aluminium particles mixtures. These values are impossible to obtain if only fine aluminium particles are used.

The "weight ratio of large particles" means the weight ratio of large particles to the whole amount of particles (large and fine). Weight ratios of 0% and 75% were employed.

The effect of the aluminium particles loadings and geometry on the composite performances was preferentially tested in A system, because this system guaranties easier processing conditions (low viscosity and high pot life).

Image processing and quantitative analysis allow the determination of the total particles perimeter divided by the total test area, $L_{A,}$, that can be mathematically related with the surface per unit volume, $S_V$ [12].

$$S_V = 4\, L_A / \pi \qquad (1)$$

The $S_V$ parameter can be used as a measure of the aluminium-resin interface area. This value depends on the aluminium concentration, particle shape and particle size distribution.

## Results

### *Processing and Packing Density*

The casting phase and the gelation process depend strongly on the metallic particle size. Particles lower than 200 µm settle down very slowly and are kept in suspension, limiting packing densities. In this case, the segregation is lower than when larger particles are used. Metallic loading, using fine class aluminium, due to viscosity limitations, reaches the maximum that can be processed, with lower particles amounts. The great advantage of using fine aluminium classes is the good ability for machining operations presented after curing.

The sedimentation process is particularly important in resins with high pot life, like the A system, where two regions with different densities are usually produced. The base presents a high powder mixture density zone, while the upper part shows a low powder mixture density. In this epoxy A system, increasing the aluminium concentration until a processing limit, has the effect of increasing the size of the high density region, and consequently the tool homogeneity. On the other hand, considering a formulation with constant large particles weight ratio, when the phr is increased, the powder packing density in the high density region can slightly decreases. This is due to the gain in viscosity, which makes difficult the packing arrangement.

Based on these preliminary experimental results, three aluminium batches were selected:

- 175 phr with fine particles class and A system;

- 150 phr with fine particles class and B system;

- 250 phr for the mixture of particles classes (fine and large) with A and B systems.

In the aluminium particles mixtures, the 75% ratio of large particles showed to be the maximum packing density of the aluminium in the resin matrix.

The effect of the metallic loadings on the processing conditions affects not only the viscosity, but also the curing time, which is about 60% longer than with unfilled resins.

The resin/hardener ratio, the hold time at a maximum curing temperature and the anti-foam addition were also studied. In A system, the resin/hardener ratio indicated by the manufacturer is not the best for the mechanical performance. Even with a 15% reduction in the hardener concentration, it is still possible to get better mechanical characteristics. Meanwhile, it is not advisable to further reduce this concentration, because the hardener acts as a strong thinner (see that the hardener viscosity is only 3.5% of the epoxy component viscosity).

### *Mechanical and Thermal Behaviour*

Aluminium-resin interface is a critical factor in the mechanical properties of the filled resins.

Using aluminium powders mixtures with large particles, reduces significantly the $S_V$ value, although high aluminium loadings are allowed. The result is a clear reduction in the mechanical properties (see table 3).

The finest powders classes show better mechanical behaviour than the mixture of fine and large powder classes. However, the elasticity modulus is lower. These mixtures still have the disadvantage of poor machinability. Nevertheless, mixtures closer to 75wt.% ratio of large particles, have high aluminium particle packing densities, promoting higher thermal conductivities and wear resistances than the resins filled with just fine aluminium class.

C system (available in a commercially filled formulation), when compared with A and B systems, shows a poor packing density (about 20% reduction - see figure 1), which explains the lowest value for the thermal conductivity. The C system costs more 40vol.% than A and B filled systems.

Unfilled B system exhibits a very good mechanical strength, elongation capacity and impact resistance. Meanwhile, when filled with aluminium, these properties are reduced to values close to the ones of the other systems. This seems to be related with the more reduced particles wetting and adhesive capacity, especially due to the high mixture viscosity of the epoxy components, originating poorer aluminium-resin interface quality.

Unlike B system, A system shows a completely different behaviour. In the unfilled state, the high cross link density, which is related with the molecular structure based on aromatic glycidyl amine, leads to a brittle network and moderate mechanical characteristics [13].

The particle geometric shape is another parameter affecting the final performance of these materials. When comparing regular shape particles (F2 class), with irregular ones (F1 class) with equivalent size distribution added to resin A (see table 2), one can verify that although they exhibit easier processing (lower viscosity), they present 8% reduction in mechanical strength and 16% reduction in impact resistance (see table 4). The crack propagation is more inhibited in irregular shape particles, which have higher surface per unit volume.

## Conclusions

Mechanical and thermal properties of aluminium filled epoxy resins depend on three parameters: aluminium concentration, particle shape and particle size distribution.

Although the mechanical characteristics of the different unfilled epoxy resins can vary significantly, after the addition of the same metallic loadings, these differences are generally reduced. The main reason for this fact lies in the important role of the aluminium-resin interface.

For the same aluminium powder class, the resins metallic loading capacity strongly depends on the mixture viscosity and the wetting capacity of the resin components.

The mechanical strength and the impact resistance are significantly reduced by the addition of large aluminium particles.

The thermal conductivity is closely related with the resins metallic loading capacity.

Aluminium loadings for high packing densities must be used in tool areas that will be not processed by machining and when the mechanical strength is not a critical factor.

The pre-filled resins, although more easily processed, present lower thermal conductivities than the resins filled by the user, and are significantly more expensive.

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## Keywords

Aluminium filled epoxies, composites, rapid tooling

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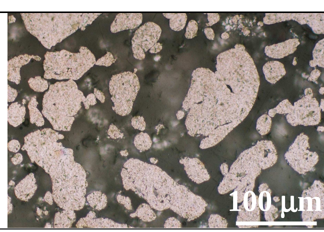
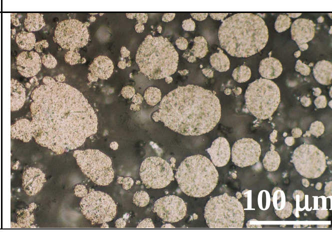
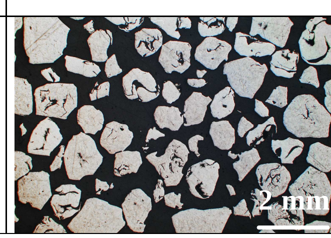
| Resin System | A | B | C |
|---|---|---|---|
| Epoxy Components | ●TGDDM = N, N, N´, N´- tetraglycidyl – 4, 4´ - diaminodifenylmethane ●butahedioldiglycidyl ether | ●Bisphénol F diglycidyl ether ●Epoxidized phenolnovolaks ● Bisphénol A- épichlorhydrin oligomer | ●Bisphénol A- épichlorhydrin oligomer; ● Epoxidized phenolnovolaks ●1,1,1 – Tris (hydroxymethyl) propano triglycidyl ether; ●hexan – 1,6 – diglycidyl ether; |
| Hardener | Cycloaliphatic polyamine | Cycloaliphatic polyamine | Cycloaliphatic polyamine |
| Mixture viscosity at 25ºC (mPa.s) | 700-900 (unfilled) | 1200-1600 (unfilled) | 6700 (filled) |
| Mixture ratio (resin / hard.) | 100 / 53 | 100 / 28 | 100 / 6 |
| Pot life | 7 – 9 h | 1 h 5 m | 1 – 2 h |
| Curing time | 65 h | 46 h | 42 h |
| Post-cure temp. | 200ºC | 120ºC | 140ºC |

**Table 1.** Technical and processing characteristics of the epoxy resins.

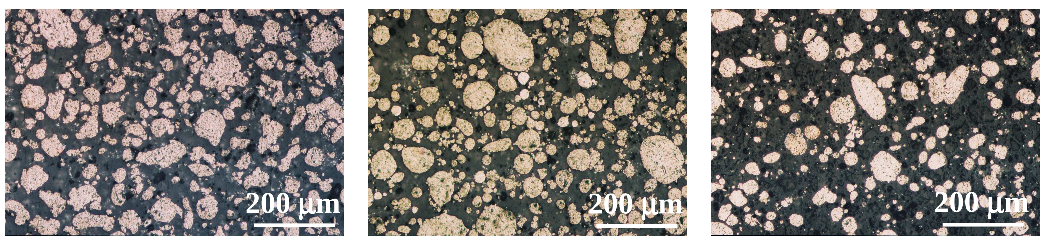
| | Fine Class | | Large Class (L) |
|---|---|---|---|
| | F1 | F2 | |
| Density | 2.74 | 2.74 | 2.72 |
| Medium size | 80 μm | 80 μm | 1400 μm |
| Particle shape | Irregular | Rounded | Rounded, with cavities and pores |
| Aspect ratio | 3.70 | 1.34 | - |
| Sphericity* | 0.60 | 0.64 | - |
| Equivalet diameter* | 19.2 μm | 17.6 μm | - |
| Surface per unit vol.* | $2.6\ \mu m^{-1}$ ** | $2.1\ \mu m^{-1}$ ** | $0.03\ \mu m^{-1}$ *** |
| Geometry |   |   |   |

*This data is a result of image processing and quantitative analysis, performed in CEMUP (Centro de Materiais da Universidade do Porto) using PAQI software.
** Aluminium filled epoxy with a 0% ratio of large particles and 175 phr
*** Aluminium filled epoxy with a 75% ratio of large particles.and 250 phr

**Table 2.** Main characteristics of the aluminium powders classes used in resin tooling.

| Epoxy System | A | | | B | | | C |
|---|---|---|---|---|---|---|---|
| Metallic filler | Unfilled | Fine (F2) | Mixture (F2+L) | Unfilled | Fine (F2) | Mixture (F2+L) | Fine (F2) |
| Flexural strength (MPa) | 66.5 | 66 | 36 | 111 | 63 | 34 | 66 |
| Flexural modulus (GPa) | 2.75 | 6.7 | 11.5 | 2.5 | 6.1 | 9.6 | 8.9 |
| Extension at break (%) | 3 | 1.3 | 0.36 | 4.5 | 1.35 | 0.4 | 0.9 |
| Charpy impact strength ($KJ.m^{-2}$) | 6.5 | 8.4 | 2 | 12 | 10 | 2 | 5.7 |
| Wear resistance (%)* | 24 | 32 | 50 | 21 | 29 | 48 | 32 |
| Thermal conductivity ($W.m^{-1}.K^{-1}$) | 0.2 | 2.1 | 3.7 | 0.2 | 1.7 | 3 | 1.1 |
| Coefficient of thermal expansion, CTE ($x10^{-5}$ºC$^{-1}$) | 7.9 | 4.7 | 3.7 | 11 | 7.1 | 6.15 | 3.5 |

**Table 3.** Mechanical and thermal characteristics of the unfilled and aluminium filled epoxy systems.




(A) (B) (C)

**Fig. 1.** Micrographs of the aluminium particles in an epoxy resin matrix: (A) in A system with F1 class powder; (B) in B system with F2 class powder; (C) in C system the packing density is clearly lower (20% reduction).

| Aluminium filler class | F2 | F1 |
|---|---|---|
| Flexural strength (MPa) | 66 | 72 |
| Extension at break (%) | 1.3 | 1.5 |
| Charpy impact strength ($KJ.m^{-2}$) | 8.4 | 10 |

**Table 4.** Mechanical characteristics of the filled A epoxy system with F1 and F2 fine aluminium classes (175 phr).