

## Impact Fracture Study of Filled Epoxy Resins

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**Abstract.** Epoxy-based composites moulds are frequently used for wax and polymer materials injection. Tri-phase materials, composed by an epoxy resin, aluminium particles and milled glass or carbon fibres were produced with better mechanical and thermal performances than the single materials, increasing the competitiveness of the epoxy rapid tooling processes. Charpy Impact tests were employed to obtain a qualitative indication of the composites toughness. The electronic instrumentation of these tests allows a more accurate differentiation of the impact behaviour of the neat and aluminium filled resins, and the tri-phase composites, and consequently, more rigorously tailor their properties.

**Oral presentation**

## 1. Introduction

The popularity of CAD 3D and rapid prototyping (RP), relatively to the traditional methods of manual production of models, are based on the capacity to produce accurate complex parts quickly. The long traditional periods of several months spent in the conception and development of a new product, previous to the decision of its acceptance by a company, can now be reduced to weeks, sometimes, even days, saving time and money. The substantial reduction in the time-to-market that is obtained, results in a great improvement on the capacity to compete in different international markets [1-4].

Although the prototypes can be used for visualization and geometric and dimensional verification, frequently, functional tests with these prototypes are not possible due to the different mechanical and thermal properties exhibited by the prototype (only a relatively narrow range of materials can be employed to produce prototypes with the RP techniques) and the manufactured product [3, 4]. Due to this fact, the RP technologies appear frequently associated with the rapid tooling (RT) technologies [5-7].

Nowadays, there are still a great number of companies that overlook the potentialities of RP and RT technologies. At international level, the evolution of these technologies is so advanced, that companies are continuously looking for the conjunction of the RP with the RT technologies, or even the rapid manufacturing (RM), seeking to accelerate the whole circuit of the industrial production. In fact, using these technologies, companies have the capacity to test a product under development in its several phases (concept models, functional prototypes, technical prototypes and pre-series), which promotes a concentration of synergies and offers a faster answer to the market needs, creating a new factor of competitiveness [2, 4].

The RT technologies, as far as their dependency from the RP model is concerned, are divided into two main groups: direct and indirect systems. Direct systems using layer manufacturing innovative technologies can directly supply the tool after some hours of machine work. On the other hand, the manufacture of a tool by the indirect methods is based on a previous fabrication of an RP model that is the starting step for the tool manufacture. After this step, the model is converted into the tool using the most appropriate process for the type of tool material to be obtained [8,9].

In general, direct rapid tooling technologies are based in very expensive equipments, high maintenance contracts and limited range of raw materials, whose availability depends essentially on the equipment manufacturer. The high global exploration costs of these processes make hard their economic viability that is restricted to the high tech industry (ex. automotive industry), where an intensive prototyping is required and where the range of alternatives options is limited. Alternatively, the indirect RT methods present the advantages of the low cost processing and equipments, and are frequently based in already known traditional technologies [1, 4].

Relatively to the tool life, one can classify the tools in three groups: soft tooling (up to 50 parts); firm tooling (between 50 and 200 parts) and hard tooling (over 200 parts) [2, 3].

For mechanical testing proposes, it is crucial that the prototypes be built in the same material and with the same manufacturing process of the production part. Some RP manufacturers propose "hard tooling" equipments. With these technologies, metal tools in steel, aluminium and copper alloys are produced with the ability to withstand thousands of cycles, behaving as a good alternative to the traditional techniques of mould making processes. Nevertheless, it will be necessary less

expensive processes, with shorter time to market, also allowing the tool validation. This need can be achieved with the Firm Tooling indirect processes, based on metal-filled resins or on metal spraying, for instance [2, 4].

In previous research [6, 10] we demonstrated the importance of using tri-phase composites, composed by aluminium particles and milled fibres, for the production of wax and plastic injection moulds. The metallic filler was added to increase the thermal conductivity of the mould, while the milled fibres allowed the improvement of the wear resistance. These two critical materials contribute to improve the moulds life and reduce the time to market of the new products to be developed.

The mechanical performance, under static and dynamic stresses conditions, also affects the moulds durability, which is a critical parameter in RT. In this context, the dynamic mechanical thermoanalysis (DTMA) and the impact behaviour of these materials were evaluated in order to understand the effect produced by aluminium particles and fibres addition to the epoxy matrix.

Using the instrumented impact test it is possible to differentiate the glass and carbon fibre reinforced composites behaviour, that otherwise would not be distinguishable. Unfortunately, impact tests are influenced by the specimen geometry and the essay equipment characteristics and consequently they are not able to evaluate independent materials characteristics. This is the reason why this research is only going to highlights the qualitative aspects of a comparative analysis of the studied materials.

## 2. Experimental Details

Epoxy resin based composites containing aluminium and milled carbon or glass fibres, with the compositions shown in Table 1, were used.

Table 1 Tested materials compositions.

Designation	A	AF	AFC	AFG
Composition (% in volume)	A - 100	A - 59 F - 41	A - 57.5 F - 38.5 C - 4	A - 57.5 F - 38.5 G - 4

A – epoxy; F– aluminium; C – carbon fibres, G – glass fibres

The epoxy resin (A) was a commercial tetraepoxide grade based in an aromatic glycidyl amine, Araldite LY5210 (Vantico, UK) with a high molecular weight [11-13]. The epoxy resin, curing agent, aluminium powder (F) and fibres (C-carbon fibres; G-glass fibres) were manually mixed and cured at room temperature for 48 h and at 40°C for 14 h, and post-cured at 200°C for 1.5 h.

The technical characteristics of the aluminium particles and milled fibres are presented in Table 2.

Table 2 Technical characteristics of the aluminium particles and milled fibres.

Dispersed phase	Manufacturer	Dimensions	Sizing
Aluminium Powder	Hexcel (France)	P200 grade	-
Milled E-glass	PPG (USA)	215/11 $\mu\text{m}$ (l/d)*	Polyvinyl acetate with silane
Milled Carbon	Toray (Japan)	63/7 $\mu\text{m}$ (l/d)*	1 wt% epoxy

\* l/d – fibre length/ diameter.

### 3. Tests

#### Dynamic Mechanical Thermoanalysis (DTMA)

The influence of the temperature on the mechanical behaviour of the epoxy-based materials was examined by dynamic mechanical thermoanalysis (DTMA) [14]. The DMTA tests were performed in a DTMA PL equipment (Polymer Laboratories, United Kingdom), using a fixed frequency of oscillation of 1 Hz. The heating rate was 3°C/minute and the samples were tested between 25°C and 275°C. The mode of stress is flexure and the fixture configuration is a simply supported beam. Sample dimensions are 45x10x5 mm (length x width x thickness).

#### Charpy impact tests

Charpy impact resistance was determined with a pendulum machine H.20 (Tensometer Ltd, Croydon, United Kingdom) with a weighing capacity varying from 0.14 to 9.07 N.

Unnotched specimens were cast in a mould, cured (according to the temperature cycle recommended by the resin manufacturer) and finished with a 320 SiC paper. For each composition, 10 specimens of 50x6x4 mm (length x width x thickness) were produced and tested.

The use of electronic equipments associated with the Charpy testing machine allows the monitoring of the load/time answer occurring during the deformation and fracture process of the test samples [15].

The instrumented tests performed with a 2.3 N weight, and the equipment was instrumented with the following accessories:

- Pulse dynamic analyser (Bruel & Kjaer 2035, Denmark);
- Piezoelectric accelerometer with 1.008 PC/m.s<sup>-2</sup> sensitivity (Bruel & Kjaer 4371, Denmark).

The initial acceleration/time curve was converted, by integration, on velocity/time and displacement/time plots, allowing the establishment of the final force/displacement curve that permits the calculation of the absorbed energy.

### 4. Results

#### 4.1. Dynamic Mechanical Thermoanalysis (DTMA)

Figure 1 shows the influence of the aluminium addition to the epoxy matrix in the thermomechanical properties. AFC and AFG composites behaviours are not represented because they present similar DMTA to the AF composites.

The peak of the  $\tan \delta$  curve is conventionally identified as the glass transition temperature [14]. This parameter allows the conclusion that the glass transition temperature of these composites occurs at about 200°C. This region, where physical properties change abruptly, is associated with the onset of short-range molecular motions.

The aluminium addition improves significantly the rigidity of the epoxy system, presenting the curves of the graph, a similar evolution across the temperature range of test. At room temperature, an increase of about 300% in the elastic or storage modulus is observed. At 200°C, there is a reduction of 73% in the neat resin, and only 63% in the AF composite. On the other hand, the  $\tan \delta$  curve of the AF composite, when compared with the monolithic resin, exhibits lower magnitudes, except in the peak of the glass transition. This fact is related with the decrease of the molecular mobility derived from the aluminium loading. In the glass transition area, the aluminium addition

originates a light displacement of this curve to high temperatures, being the  $\tan \delta$  peak more pronounced.

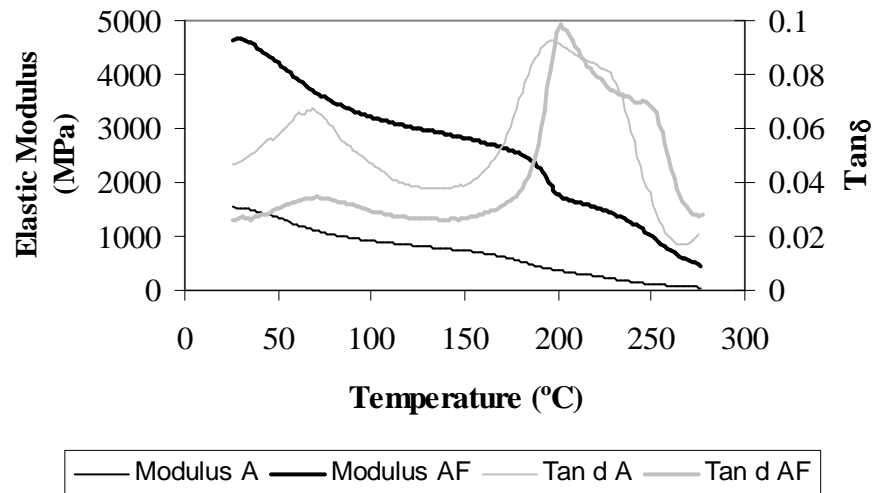


Figure 1 Neat resin A and aluminium filled epoxy (AF) DMTA (dynamic mechanical thermoanalysis) results. Elastic modulus is black and  $\tan \delta$  is grey.

## 4.2. Charpy Impact Tests

### Fractograms

The composite resistance depends on the combination of the resin properties and on the critical interface strength. When the stresses reach the critical value, the composite fails through particle debonding and pull-out in the crack propagation trajectory. This type of failure, where load transfer does not occur, is characteristic of an intergranular fracture.

In A system, the impact resistance increased about 14% with the metallic filler, which is certainly related with a good interface adhesion (Figs. 2 and 3). The A neat resin exhibits a brittle molecular structure and the aluminium particle addition promotes a new energy dissipation mechanism which is obtained through the particle pull-out. This mechanism controls the material behaviour and is responsible for the improvement in resistance.

A neat resin shows a brittle behaviour and the force/ displacement curve is free of fluctuations, which indicates that the crack is quickly propagated through the material without significant resistance (Fig. 3). The force/displacement curve is sharp-pointed and is characterized by a maximum load of 445 N.

The aluminium addition to the A resin tends to improve, although slightly, its toughness (Figs. 2 and 3). The maximum force is practically unchanged, however, higher energy dissipation is obtained. The force/displacement curve exhibits now periodic fluctuations. These fluctuations show that the aluminium dispersed phase acts as an interference mechanism on the crack propagation velocity. The aluminium particle addition introduces this interference mechanism combined with the interface resistance. The influence of the interface aluminium particles/epoxy in macroscopic properties is highlighted in previous research [16].

Fibre addition introduces an extra energy dissipation mechanism. Nevertheless, due to processing difficulties, the fibre concentrations and the fibre lengths employed are small, reducing its reinforcement capacity. Furthermore, complex stress concentrations regions are introduced due to the randomly oriented fibres [17]. The improvement obtained in the impact resistance is not meaningful, as one can see in Fig. 2.

Fragmentation tests were performed with the glass and carbon fibres filaments to determine the fibre/epoxy interfacial shear strength (ISS). It was possible to conclude that the carbon fibres ISS value was 90% higher than in the glass fibres [18]. The failure mechanisms of the two types of fibres was different, with a dominant matrix failure in the carbon fibre/epoxy, while in the glass fibre/epoxy was only detected an interfacial type of failure. Nevertheless, the better performance of the carbon fibre/epoxy interface does not seem to significantly enhance the mechanical toughness, except for the wear resistance, that is significantly improved [19].

The addition of fillers (including milled fibres), despite the good interfacial properties with the matrix, frequently does not contribute to a mechanical improvement. This is due to the stress concentrations, promoted at a microscopic scale, by the different mechanical and thermal properties of the two phases.

Although the impact resistance of the composites with carbon or glass fibres is indistinguishable, their typical fractograms show that these two hybrid composites have a tendency to behave quite differently, with the AFC composite presenting a higher deformation capacity. For the same fibre volume fraction, the carbon fibres are more numerous and exhibit a higher interface area, which could explain the delay in the fracture process. Glass fibres tend to give, for the maximum load, the same characteristic displacement of the aluminium filled composites, however, demanding a higher force for crack propagation.

### Fracture Surfaces

Polymers do not exhibit the same brittle fracture as metallic materials. At high magnifications, it is always possible to see plastic deformations in films and deformed fibrils, sometimes only

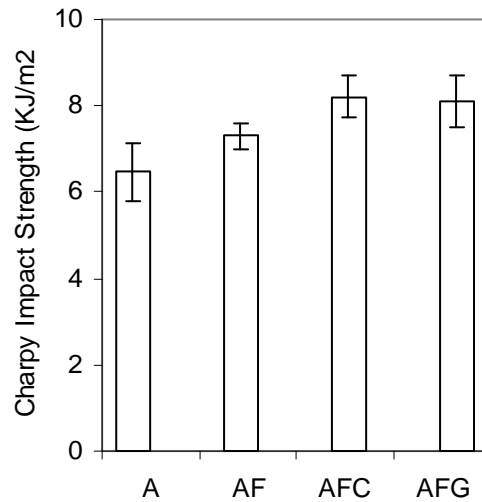


Figure 2 Charpy Impact Strength results of the studied materials.

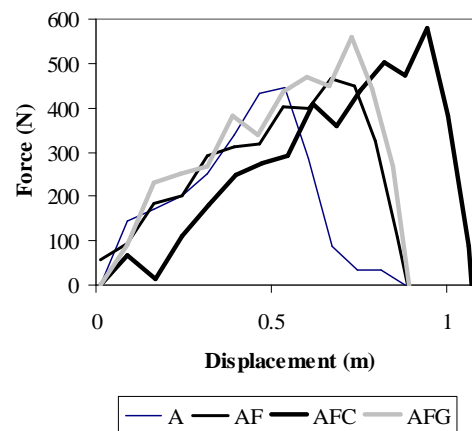


Figure 3 Characteristic fractograms of A, AF, AFC and AFG.

possible to see on a micrometer scale. Oval lids or torn-open blisters, steps and striped patterns can also be found [20].

These microstructures, that are located in a narrow stressed micrometric layer of the fracture surface, give clear information about the initiation point and fracture propagation directions. The formation of these brittle failure bands is due to the crack crossing over heterogeneities.

The neat A resin shows a fracture surface significantly less texturized than the respective composites. As the crack propagates, the local fracture front divisions that can be detected rapidly join in a single front, originating a surface with a predominantly continuous morphology.

Epoxy resins reproduce the fine details detected at a microscopic scale. The texture of the cavities from where the aluminium particles were pulled-out is very well reproduced. Figure 4 shows the granular surface of the particles, which is the result of the crystallization process occurred during the alloy solidification (gas atomisation).

AFG and AFC composites exhibit very complex fracture mechanisms, including matrix rupture, particle and fibre pull out, fibre delamination, fibre rupture and residual stress concentrations around the fillers (Fig. 4). The surface fracture near the fibres is particularly texturized showing that fibres influence strongly the composite mechanical behaviour.

## 5. Conclusions

The tools produced by this indirect rapid tooling process do not survive as long as the conventional metallic tools, however they are extremely adequate to produce functional prototypes and pre-series with a better cost/time factor than the metallic tools obtained by traditional methods.

The instrumented Charpy tests used in this work allow the monitoring of the load/time answer of composite materials, supplying important data about their impact behaviour. These tests are especially useful to qualitatively compare different materials, with the same dimensions, tested in the same conditions and using the same test equipment. In this research it contributed to a better understanding of the influence of the aluminium particles and carbon and glass fibre additions to different epoxy resins and to differentiate the contribution of the milled carbon fibres from the milled glass fibres.

Composite epoxy based materials were produced and optimised for a specific Rapid Tooling application, namely, moulds to inject pre-series of thermoplastic parts. In previous research, it was found that AFG and AFC composites show better thermal and mechanical properties than conventional AF composites. Particularly, AFG exhibits an outstanding wear resistance and is easier to process than AFC composite. In this paper it was shown that the impact resistance of the moulds depends on complex energy dissipation mecha-

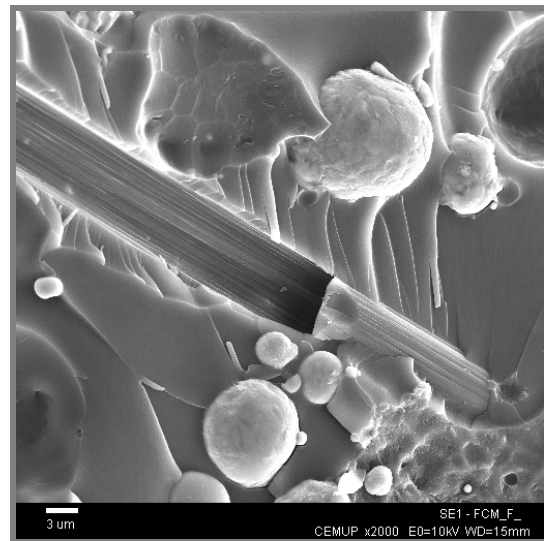


Figure 4 Typical SEM fracture surface of the AFC composite.

nisms, where the interface properties and the particles and milled fibres stress concentrations play an important role on the control of the composite fracture behaviour.

Impact fracture resistance results of the hybrid composites show that the good adhesion between fibres and epoxy matrix can be hindered by the complex stress concentrations around the fibres.

SEM images of the fracture surfaces allow the reinforcement and complement of the data obtained with the instrumented Charpy mechanical tests.

## References

1. C. K. Chua, K. F. Leong and C. S. Lin, *Rapid Prototyping – Principles and Applications*, 2<sup>nd</sup> Ed., World Scientific, Singapore, 2003.
2. T. Wholers, *Wholers Report 2003*, Wholers Associates, Colorado, USA, 2003.
3. P. Vasconcelos, F. J. Lino, R. Neto, *O Fabrico Rápido de Ferramentas ao Serviço da Engenharia Concorrente*, Tecnometal 136, p. 17, 2001.
4. F. J. Lino, F. Braga, M. Simão, R. Neto, T. Duarte, *Protoclick – Prototipagem Rápida*, Protoclick, Porto, Portugal, 2001.
5. P. Vasconcelos, F. J. Lino, F. V. Hattum, R. Neto, *Mathematical Models for Particulate Filled and Milled Fibre Reinforced Composites*, Advanced Materials Forum II, p. 742, 2004.
6. P. Vasconcelos, F. J. Lino, R. Neto, *Utilização de Fibras Moídas no Fabrico de Ferramentas de Matriz Polimérica*, in: Proceedings of 2<sup>as</sup> Jornadas Politécnicas de Engenharia, November, EST Setúbal, Portugal, 2002.
7. P. Liaw, *Impact Toughness Testing and Fracture Mechanics*, in: Howard Kuhn, Dana Medlin (Eds.), *Mechanical Testing and Evaluation*, Vol. 8, ASM Handbook, p. 561, 2000.
8. J. Williams, *Rapid Tooling for Plastics Injection Moulds, Application and Decision-Maker Tools*, TCT Conference '99, Nottingham Royal Moat House, October 1999.
9. N.P. Karapatis, *Direct Rapid Tooling: a Review of Current Research*, Rapid Prototyping Journal, Vol.4, nº2, p. 77, 1998.
10. P. Vasconcelos, F. J. Lino, F. V. Hattum, R. Neto, *Mathematical Models for Particulate Filled and Milled Fibre Reinforced Composites*, Advanced Materials Forum II, p. 742, 2004.
11. L. Matejka, K. Dusek, *Mechanism and Kinetics of Curing Epoxides Based on Diglycidylamine with Aromatic Amines. 1. The Reaction of Diglycidylaniline with Secondary Amines*, Macromolecules 22, p. 2902, 1989.
12. L. Matejka, *Amine Cured Epoxide Networks: Formation, Structure and Properties*, Macromolecules 33, p. 3611, 2000.
13. B. A. Rozenberg, *Kinetics, Thermodynamics and Mechanism of Reactions of Epoxy Oligomers with Amines*, Adv. Polym. Sci. 75, p.113, 1986.
14. M. P. Sepe, *Dynamic Mechanical Analysis for Plastic Engineering*, Plastic Design Library, 1998.
15. P. Liaw, *Impact Toughness Testing and Fracture Mechanics*, in: Howard Kuhn, Dana Medlin (Eds.), *Mechanical Testing and Evaluation*, Vol. 8, ASM Handbook, p. 561, 2000.
16. P. Vasconcelos, F. J. Lino, R. Neto, P. Henrique, *Contribution of the Phase-Matrix Interface in the Behaviour of Aluminium Filled Epoxies*, Advanced Materials Forum II, p. 635, 2004.
17. P. K. Mallick, *Particulate and Short Fibre Reinforced Polymer Composites*, in: A. Kelly and C. Zweben Eds., *Comprehensive Composite Materials*, Vol. 2, Elsevier, p. 291, 2000.
18. P. Vasconcelos, *Fabrico Rápido Indirecto de Ferramentas Compósitas a Partir de Modelos Obtidos por Prototipagem Rápida*, PhD Thesis, Faculdade de Engenharia da Universidade do Porto, Porto, Portugal, to be submitted in October, 2004.
19. P. Vasconcelos, F. J. Lino, A. M. Baptista, R. Neto, *Tribological Behaviour of Epoxy Based Composites for Rapid Tooling* (Accepted in the Journal of Wear), September, 2004.
20. L. Engel, H. Klingele, G. Ehrenstein, H. Schaper, in: *Atlas of Polymer Damage, Surface Examination by Scanning Electron Microscope*, Wolfe Science Books in association with Carl Hanser Verlag, 1982.

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