# PROCESSING GLASS-CERAMIC MATRIX COMPOSITES BY LIQUID MOULDING: CHARACTERISATION OF THE RHEOLOGY OF A RESIN DERIVED FROM A GEOPOLYMERIC SYSTEM

A. Farrugia[1*], G. Dusserre[1], T. Cutard[1], M. Rollin[2]

[1]*Université de Toulouse, Mines Albi, INSA, UPS, ISAE, ICA (Institut Clément Ader), Campus Jarlard F-81013 Albi cedex 09 France*
[2]*Pyromeral Systems, 13 route d'Ognon F-60810 Barbery France*
**Anais.FARRUGIA@mines-albi.fr*

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**Abstract**
*The present paper reports the results of the study of an inorganic resin in order to find the best conditions to obtain the lowest viscosity to produce a structural glass-ceramic matrix composite by liquid moulding. Firstly, rotational and oscillatory measurements were done on a rheometer with cone-plate and plate-plate geometries. The studied parameters were resin aging, shear rate, temperature and water content. Secondly, tensile tests on some composites were carried out to study the influence of the resin's water content. Results show that the resin conservation in a frozen state cannot reach a period larger than few months. Besides, the resin has a shear thinning behaviour but the viscosity is constant when the shear rate is high. Moreover, a competition is noticed between the matrix microstructure changes due to a larger resin's water content and a better infusion thanks to a lower viscosity.*

## 1 Introduction

A new class of glass-ceramic matrices for structural composites was developed for continuous thermal exposure applications. These new matrices come from inorganic thermosetting polymers. One advantage of this family is that hardening occurs at temperature lower than 100°C. Thanks to their inorganic nature, these new matrices give composites with high temperature resistance and structural properties comparable to conventional ceramic matrix composites. As a consequence of the low temperature hardening of these matrices, composites are manufactured using the conventional processing routes of organic matrix composites like prepreg process. So, these materials can bridge the gap between organic matrix composites and ceramic matrix composites. But, to be competitive, easy and cost effective process technologies must be used. Liquid moulding, such as LRI or RTM, seems to be a convenient solution. However, both the viscosity of those inorganic polymers and the effect of process parameters on the composite mechanical properties must be investigated. The research leaded at Institut Clément Ader in Albi (France) focuses on a unique resin synthesized by the French company Pyromeral Systems®. This resin is derived from a geopolymeric system. These systems are synthesized thanks to a chemical reaction between an aluminosilicate material and a silicate solution in an alkaline environment [1]. The exact mechanism of this reaction is not fully understood yet but it is believed to consist of the dissolution of solid alumino-silicate particles in the solution, their diffusion, the polycondensation between solid particles and the

silicate solution and finally the hardening of the gel phase [2]. A lot of researches aimed at having a better comprehension on geopolymers but most of them focus on its solid state. The particularity of the resin is that it gives a glass-ceramic matrix. So, results cannot be related to the system investigated here. The results of few studies that have considered the liquid state of geopolymer resins describe them as Bingham fluids [3,4] whose viscosity is influenced by chemical composition, temperature and resin history [4]. The aim of this work is to find the best conditions to obtain a viscosity as low as possible in order to produce a structural composite by a liquid moulding way. As the resin is an aqueous suspension of mineral raw materials, the first way to decrease its viscosity is to increase the water content in order to keep an environmentally friendly material. That is why the influence of water dilution is investigated. This paper reports experimental results about the rheology of the resin and the mechanical behaviour of the glass-ceramic matrix composites manufactured by prepreg process using this resin. Firstly, continuous and oscillatory shear viscosity measurements were performed both on a plate-plate rheometer and a cone-plate rheometer, at temperatures ranging from 10°C to 100°C. The effect of resin aging, shear rate, temperature and water content were studied. Besides, the gelation time was estimated. Indeed, the glass-ceramic matrix is obtained thanks to a heat treatment but composite must be removed from the mould first. So, resin must be hardened in the mould and gelation time is a key parameter. Secondly, tensile tests on some glass-ceramic matrix composites reinforced with carbon fibres were carried out in order to study the influence of the resin's water content on the mechanical behaviour.

## 2 Materials

The studied resin is an inorganic polymer synthesized by the French company Pyromeral Systems®. This resin is derived from a geopolymeric system. The composition is fixed and confidential. Between the manufacture and the use of the resin, it is frozen at −18°C. The resin is characterised as manufactured and with an addition of 2wt% water. Composite materials are manufactured by the Pyromeral's prepreg process. The reinforcement used in this study is composed of 6 layers of woven fabrics made from carbon fibres. Thanks to a specific and confidential heat treatment, a glass-ceramic matrix is obtained and provides a composite for continuous thermal exposure applications. The composites are manufactured from resins with different water contents from 0wt% to 5wt% with 1wt% increments.

## 3 Experimental procedure

### *3.1 Rheological measurements*

Flow and oscillatory shear tests are performed using a Rheostress 600 (Thermo Electron) rheometer. The flow test geometry consists of a 1° truncated cone-plate with a gap of 0.054 mm. The oscillatory test geometry consists of parallel plates with a gap of 1 mm. Both geometries have smooth surfaces and a diameter of 35 mm. The frequency of the oscillatory shear tests is maintained constant at 1 Hz throughout the rheological testing. The resin is frozen at −18°C between the manufacture and all the tests described bellow. The first rheological measurements aim at studying resin aging. These oscillatory tests allow resin complex viscosity to be determined at room temperature and are carried out periodically during several months with a controlled strain of 1%. Each sample tested has never been defrosted before. The second rheological campaign aims at studying resin sensitivity to shear rate and temperature. Flow tests are carried out and determine the viscosity for three temperatures (10°C, 15°C, 20°C). At these temperatures, the reaction kinetics is supposed to be low. A strain sweep is applied by straining the resin sample from 0.01 $s^{-1}$ to 200 $s^{-1}$, and the resulting stress is recorded. The strain sweep applied is represented on figure 1. On each step, measurement occurs when the stress is stabilised. Each test lasts no more than a few minutes.

So, it is supposed that no chemical evolution occurs. The same resin sample is tested once ($t_0$) and 30 minutes later ($t_0$ + 30 minutes). The third rheological campaign aims at evaluating the complex viscosity change during cure, at different temperatures. The measure of the viscosity from liquid state to solid state is investigated through oscillatory tests. Strain is maintained at 3% to stay in the linear range. Considered temperature levels are 60°C, 70°C, 80°C, 90°C and 100°C, for undiluted resin and a resin diluted with a water content of 2wt% and, another test is carried out at 20°C on the undiluted resin. Measurements last until the resin hardening.

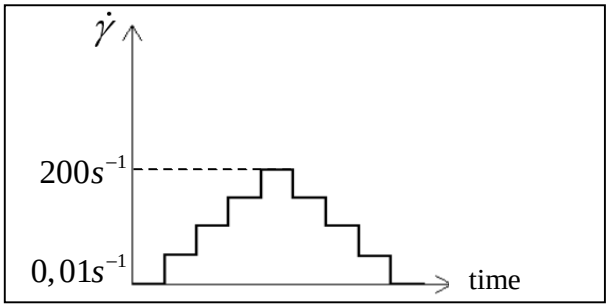


**Figure 1.** Variation of shear rate with time during flow tests

*3.2 Mechanical tests*

Cyclic tensile tests are conducted using a computer-controlled 250 servohydraulic testing machine (810MTS) equipped with hydraulic grips. The tensile tests are performed at room temperature under displacement control at a displacement rate of 1 mm per minute. A 30 mm gauge length extensometer is used to measure the sample strain. Specimens are loaded up to 150 MPa during the first cycle and then, each cycle stress increases by 50 MPa, until coupons fail. Stress-strain data are recorded during the loading. Specimen total length is 200 mm and aluminium tabs of 50 mm-length are bonded.

## 4 Experimental results

*4.1 Rheological measurements*

The first rheological study shows that at the beginning of the resin life, the complex viscosity decreases progressively from 23 Pa.s to reach 1 Pa.s. This low viscosity is stable before it begins to vary. Hence, the resin becomes unusable. Its texture changes and the resin gets closer to a gel than a liquid. These results, presented on figure 2, permit to conclude that the best period to use the inorganic resin is during its domain of low and stable viscosity. The resin tested in all the following results has the more favourable aging time.

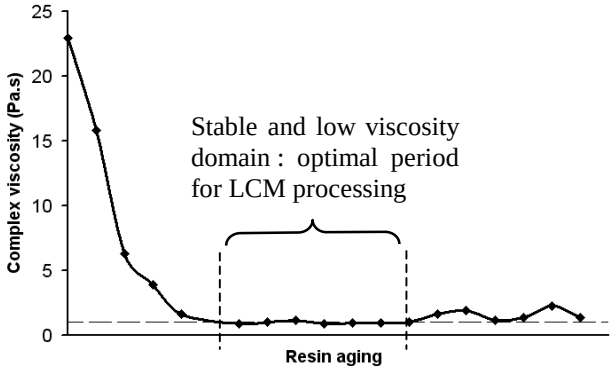


**Figure 2.** Variation of complex viscosity with aging time of the resin conserved at –18°C (time scale hidden)

The second rheological study gives rheograms at temperatures of 10°C, 15°C and 20°C and at different reaction levels. All rheograms show the same behaviour. In the low shear rate range, between 0.01 $s^{-1}$ and 10 $s^{-1}$, the resin undergoes a shear thinning effect. At higher shear rates, the viscosity is quite constant. Figure 3 shows the rheograms obtained for the undiluted and the 2wt% diluted resins at 15°C and $t_0$. Only constant viscosity domains are represented for some curves (at 20°C and at $t_0$ + 30 minutes) to have a clearest figure. Thus, the evolution of constant viscosity domain with time for the 15°C and 20°C temperatures can be investigated. In any cases, only the shear rate decrease is presented.

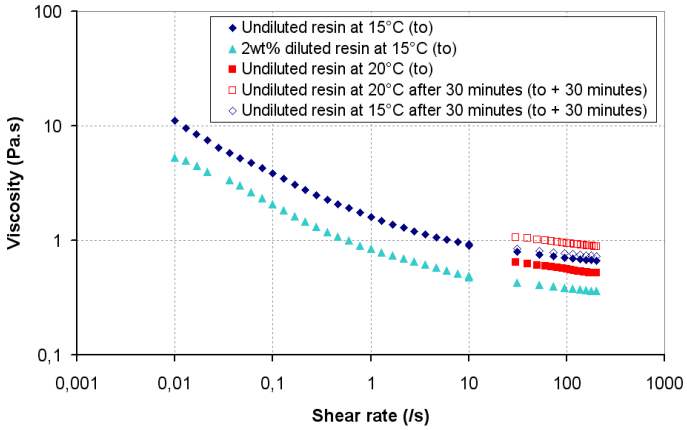


**Figure 3**. Typical rheograms for undiluted resin and 2wt% diluted resin at 15°C and partial representations of rheograms for undiluted resin at 15°C and 20°C, at $t_0$ and $t_0$ + 30 minutes

Temperature of 15°C offers a resin with a stable behaviour with time. Indeed, viscosity stays quite the same during at least 30 minutes (evolution from 0.67 to 0.73 Pa.s). At 10°C, the same behaviour can be noticed (evolution from 0.79 to 0.83 Pa.s) but viscosity values are higher than at 15°C. At 20°C, the viscosity is less stable because it increases from 0.52 Pa.s to 0.88 Pa.s in only 30 minutes. Moreover, rheograms of the 2wt% diluted resin show that rheological behaviour under various shear rates stays unchanged compared to the undiluted resin. Besides, the diluted resin viscosity in the high shear rate is 0.36 Pa.s at 15°C and it is approximately two times lower than the undiluted resin which viscosity is 0.67 Pa.s at 15°C.

Gelation of the resin is studied thanks to the third rheological campaign. All the results show the same behaviour. The figure 4 gives an exemple for 100°C. Viscosity firstly goes up, still-staying low, but after a period dependant of the temperature, the curve rises to reach a plateau which means the sample is in a solid state. The storage modulus G' evolves similarly but the loss modulus G'' behaves differently. G'' values are firstly superior to G' values. G'' increases and reach a pick after G' begins to increase and thus, G'' becomes lower than G'. Then, G'' values decrease to finally stabilize. The gelation of the resin samples is assumed to be at the intersection of the loss modulus and the storage modulus curves [5].

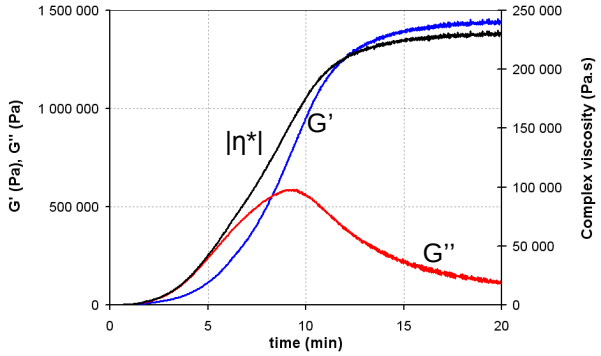


**Figure 4.** Typical oscillatory test results : case of the undiluted resin tested at 100°C until hardening

*4.2 Mechanical tests*

The tensile test results show that composites manufactured from undiluted resin have a mainly elastic and quasi brittle behaviour. The initial elastic modulus is around 70 GPa and the failure stress is around 290 MPa. Composites made from diluted resins up to 2wt% of water content keep constant their behaviour and elastic modulus value, but failure stress decreases. When water content is 3wt% or more, composites exhibit an enhanced damage capacity as presented on figure 5. The initial elastic modulus is decreased and close to 65 GPa but the failure stress is not more affected, compared to lower dilution rates.

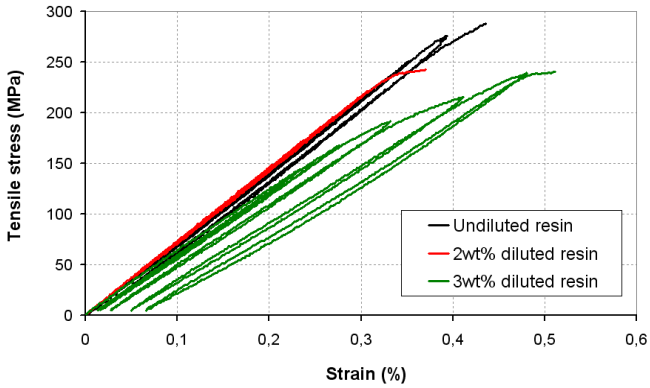


**Figure 5.** Influence of dilution on the tensile behaviour of glass-ceramic matrix composite materials

## 5 Discussion

*5.1 Rheological behaviour of the resin during LCM*

The viscosity variations during its storage at –18°C are obviously related to the resin chemical reactions. The first reaction step is the dissolution of solid particles [2]. This could be associated to a viscosity decrease. Consequently, in order to have the lowest viscosity, the resin needs to maturate. Dilution also permits to have a lower viscosity, if needed. Besides, the viscosity needs to be stable during the whole process. So, the resin temperature needs to be controlled and maintained around 15°C or less. At 20°C, results show that the reaction kinetics is too important to use such a resin in a LCM process.

*5.2 Low temperature curing of the resin*

Figure 6 shows that the gelation time logarithm is linearly dependant to the inverse of the temperature. Gelation time seems to follow an Arrhenius law which could demonstrate the hardening process of the resin would be thermally-activated. Activation energy would be 54 $kJ.mol^{-1}$ for the undiluted resin and 60 $kJ.mol^{-1}$ for the 2wt% water content resin. Consequently, the reaction mechanism of the resin seems to remain quite unchanged after dilution. The temperature of the low temperature curing step (gelation step) is thus expected not to affect drastically the properties of the resulting composite. Moreover, the high

temperature curing (postcuring) may erase these weak material differences. This is particularly interesting since it allows large parts to be manufactured without paying a particular attention to the homogeneity of the temperature.

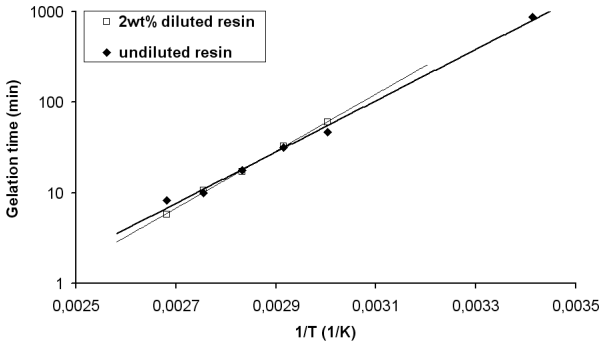


**Figure 6.** Gelation time versus the inverse of temperature

*5.3 Influence of dilution on the tensile behaviour*

Adding water seems to be a good way to decrease viscosity without changing the chemical reaction but consequences on composite materials must be investigated. The results of the first tensile tests show that dilution decreases mechanical properties like elastic modulus and failure stress but enhances the damage capacity of composites. This is a very wished behaviour for safety reasons since it may prevent brittle failure of the part. This is obviously due to microstructure changes involving a different crack propagation. Microstructure changes will be investigated in further studies.

*5.4 Discussion on the gelation time determination*

The gelation time is assumed to be located at the point where G'=G". Some authors [5] think that the gelation occurs when the rheological behaviour is independent of the test frequency. In the field of organic resins, both criterion are valid because determined gelation times are close. But, this needs to be checked for the system studied here. Tests with different frequencies must be carried out to conclude about the validity of the gelation time determination criterion.

## 6 Conclusion

Rheological characterisation of a resin derived from a geopolymeric system makes it possible to obtain a better knowledge of its behaviour for processing glass-ceramic matrix composites by liquid moulding way. The resin needs chemical maturation to reach the lowest viscosity values and its conservation in a frozen state cannot reach a period larger than a few months. Furthermore, temperature permits to decrease the viscosity but needs to be less than 20°C to keep low reaction kinetics. The study of the influence of resin water dilution permits to know that the system stays unchanged. Morevover, viscosity decreases with the dilution rate which allows a better filling of the fibre reinforcement. And, damage and strain capacities of composites are improved. However, elastic modulus and failure stress are affected by the dilution of the resin. Hence, dilution is interesting because it helps impregnation and it involves a non linear behaviour of the composites. The results of the mechanical tests show a competition between the mechanical properties due to the larger resin's water content and a better infusion thanks to a lower viscosity. A compromise must be found between high mechanical properties and impregnation ease. This research is the first step to enable manufacturing of competitive structural composites able to bear up continuous thermal exposure such as in aircraft parts located close to engines.

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