MICROMECHANICAL AND MICROSPCOPIC EFFECTS OF PREPROCESSING ON INTERFACIAL SHEAR STRESS OF GLASS FIBER-CYANATE ESTER RESINS COMPOSITE

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SUMMARY

In this study, effects of process conditions before cure stage are investigated by means of different approaches. Microbond pull out test is used to characterize Interfacial Shear Stress at different resin conversion and after preprocesses. It's shown that before gel point IFSS depends but on resin whereas at high conversion, IFSS is system depend. IFSS versus conversion show a S-shaped curve. Vacuum process before cure stage magnified IFSS by 1,5-1,7. Shrinkage of microdroplet at cooling has been also simulated. Effects of interphase thickness and Young modulus are studied. Then, dielectric spectroscopy is used to characterize interpenetrating mechanism between sizing and matrix. Effects of process stage are overlaid and analyzed in case of dielectric relaxation and ionic conductivity measurements. To conclude, an interaction mechanism between sizing and matrix is proposed.

KEYWORDS: Pull out, vacuum effects, sizing, dielectric spectroscopy, shrinkage, thermosetting resin.

INTRODUCTION: Microbond pull out test was first designed to reach the Interfacial Shear Stress (IFSS) of Glass fiber-thermoplastic composite materials. It's now widely used as a testing tool to characterize evolution of fiber-thermosetting[1] resin system interfacial properties.
For instance, Feller and al[2] have recently used this approach to characterize effects of different kind of sizing material between E glass fiber and polypropylene. S. Pillut and al[3] have investigated hydrolytic aging of interface in case of silice fiber and propargyl chromene thermosetting resin. This micromechanical test is now considered as a reliable tool to study evolution of interfacial properties of monofilament composite materials.
We have chosen this test to characterize interface between D Glass fiber and cyanate ester thermosetting resin. We are investigating a new approach which consist in studying effects of process conditions before and during cure stage. Conversion and kinetics effects on IFSS are overlaid. In order to closely relate industrial processing, a low pressure stage is applied to the system before curing. Duration of low pressure stage and effects on IFSS are investigated. This study is based on different approaches, a micromechanical one (microdroplet pull out test), a numerical one and a molecular one by means of dielectric spectroscopy.

EXPERIMENTAL

Materials and technics

In this study, a D Glass fiber is used with a given coupling agent. Two kinds of commercial cyanate ester resins from CIBA are used:

- AROCY M: Bis(4-cyanato-3,5-dimethylphenyl)methane;
- AROCY B: 2,2'(4-cyanatophenyl)isopropylidene.

To evaluate kinetics of curing, a FTIR Nicolet spectrometer has been used. Curing is extrapolated from spectrum by measuring the evolution of cyanate unreacted band at 2270 cm^{-1}.
The 3000-2800 cm^{-1} region corresponding to the methyl vibration is considered as the reference band. resin conversion is calculated as area of cyanate band normalised by area of methyl reference band at given conditions divided by the same rate at initial time.
Tg values determined by DMA are measured by a visco analyzer RSA 2 from Rheometrics. Experimentation have been conducted with the dual cantilever tool at 1Hz and 2K/mn heating rate.
Fiber are pulled out of the microdroplets at a rate of 2 mm/mn, using an Adamel Lhomargy DY35 tensile tester and a 10 N force cell.
Dielectric measurements were performed with a DEA 2970 dielectrometer from TA Instruments. A ceramic single surface sensor based on a coplanar interdigitated-comb configuration of electrodes were used.

IFSS versus conversion

In order to obtain the best mechanical properties, industrial processing used to curing system till maximum conversion. In this first part, effects of conversion on IFSS are studied. Several parameters are investigated, such as kinetic, temperature of cure and isothermal curing time.
Conversion is extrapolated from FTIR spectroscopy measurements, using the internal reference method. Both resin and microdroplet curing are studied.
Kinetic curves are fitted by a Stutz and al [4-5] first order model, considering Tg effects at the end of reaction. Kinetic constants are calculated from the slope of kinetic curves at initial time versus temperature. DMA measurements coupled with microscopic FTIR measurements show the evolution of Tg versus conversion. In the same way, conversion of microdroplets is obtained by FTIR measurements.*ilament* break before debonding.

Table 1 shows excellent correlation between resin and microdroplet curing. Since resin used is a catalyzed system, cyanate ester resin curing kinetics does not depend on environmental media. Then, all over this study, microdroplet conversion will be considered as resin conversion as describe below.
IFSS is obtained via the microbond pull out test. As shown on *Figure 1*, IFSS remains nearly constant at low conversion and increase strongly near the gel point of the system, α=0,6. IFSS cannot be measured for conversion above 0,6 since the monofilament break before debonding.

Table 1: correlation between conversion of resin and microdroplet conversion

Isothermal 180°C	Resin Conversion	Microdroplet conversion
30 mn	0.4	0.35
60 mn	0.52	0.51

So, a second type of fiber has been tested in order to get IFSS at conversion higher than gel point. An aramid fiber has been chosen. *Figure 2* shows an S-shaped curve for evolution of IFSS. At low conversion, IFSS is still constant. The measured value of IFSS is the same as the observation in case of D-Glass fiber. Strong evolution occurs in gel point area. For conversion just above gel point, IFSS remains nearly constant. As shown on *Figure 2* , no kinetic effect occurs in case of adhesion mechanism. By increasing curing temperature, kinetic constant increase. No significant effects on IFSS are overlaid. In other words, same IFSS is obtained at given conversion whatever kinetic involved. IFSS is only depending on conversion.

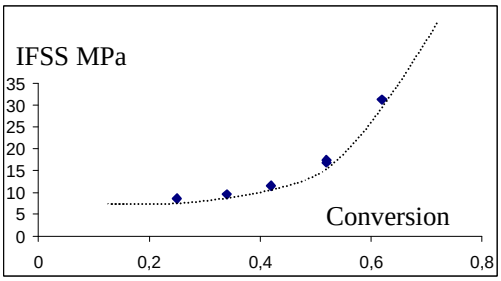

Figure 1: D Glass fiber: IFSS versus conversion

Same results have been obtained on D-Glass fiber using Arocy B30 cyanate ester resin. As reported by Hamerton[6], Arocy B resin kinetics are twice as Arocy M ones. IFSS evolution is resin nature independent at low conversion despite the fact that curing kinetics are different.

As mentioned previously, an interesting fact is that IFSS value at low conversion is nature fiber independent. Whatever system involved, IFSS seems to depend but on resin. In the same way, and as usually used, microbond pull out test at high conversion is fully fiber matrix system dependent. Higher is IFSS, stronger are interfacial interactions and better is the system involved. As will be developed further, debonding seems to be matrix dependent in the first stage, and fiber/matrix system dependent at high conversion.

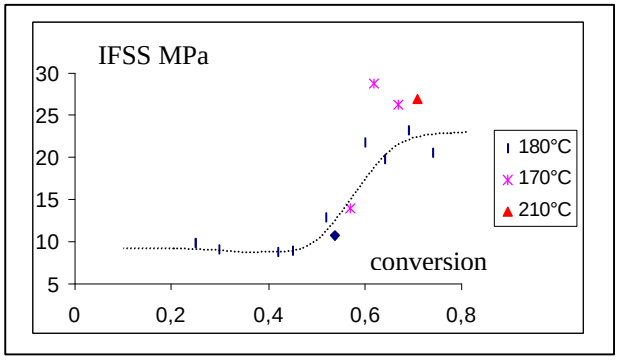

Figure 2: Aramid fiber: IFSS versus conversion

Fracture profile and characterization

As mentioned in experimental part, microdroplet evolution are recorded during pull out test. Two kinds of failure are observed. At low conversion, interface breaks as drawn on *Figure 3*. Debonding results from matrix fragile breaking. At high conversion, linear interfacial failure are observed. *Figure 4* presents load curve type recorded in this kind of failure. It looks like a "stick slip" phenomenon, characteristic of a typical two dimensional interfacial effect.

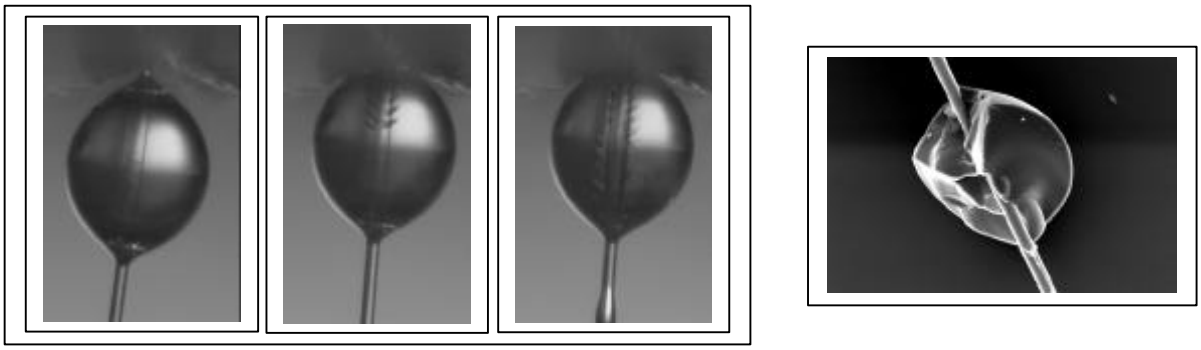

Figure 3: Fracture profile at low conversion

In order to characterize interfacial failure type, sample are observed by SEM. Debonded microdroplet are observed at low and high conversion. Whatever conversion, adhesive interfacial failure is overlaid as shown on figure 5.

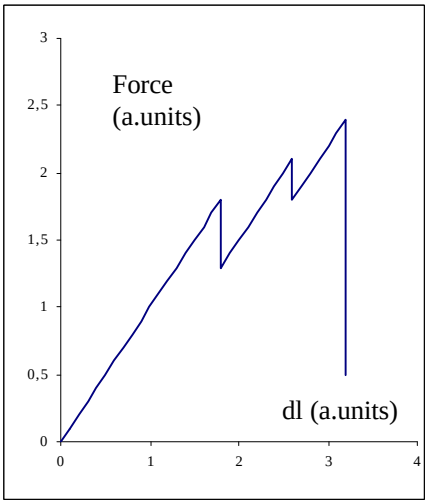

Figure 4: Load curve during pull out at high conversion

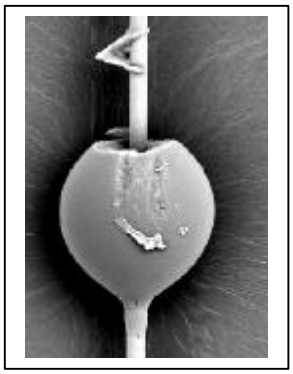

Figure 5: Fracture profile

Fracture mechanism

As regard to previous results, an adhesion mechanism is proposed considering conversion effects.
At low conversion, failure is due to matrix fragile fracture. In this case, matrix is the limiting parameter. Before gel point, resin is organized as microgel network. Internal matrix cohesion is low. During pull out test, resin breaks in the highest shear stress area, near fiber matrix interface.
As system reaches gel point, internal matrix cohesion is achieved by ultra high molecular weight macromolecule development. Matrix mechanical properties are then strong enough to resist under stresses induced by the pull out test. In this case, interface interactions become limiting. That's why a 2 dimensional failure is observed at debonding.
As a conclusion, gelification appears as a critical parameter in composite process, in case of adhesion and fracture mechanism.

In order to characterize interfacial properties at high conversion, a numerically way of investigation has been studied.

Shrinkage effects

IFSS could result from matrix shrinkage by cooling microdroplet after cure stage. In this part, we try to quantify shrinkage effects in case of adhesion mechanism.
Microcracking experimentation on monofilament composite have shown strong shrinkage influence, as reported on Figure 6. In Case of Aramid made microdroplet, same fracture shape on fiber is observed. This means that even on microdroplet, shrinkage has a strong influence.

So, in order to quantify shrinkage influence on IFSS, a numerical method has been investigated. Droplet profile are related by a wetting model[7]. Considering abusively stress relaxation of the system during cure stage, microdroplet is numerically cooled form 180°C to 20°C. No effects in residual shear stress are noticed by varying droplet shape in case of wetting angle and droplet diameter. Only thermal expansion coefficient has a strong influence on shear stress amplitude.

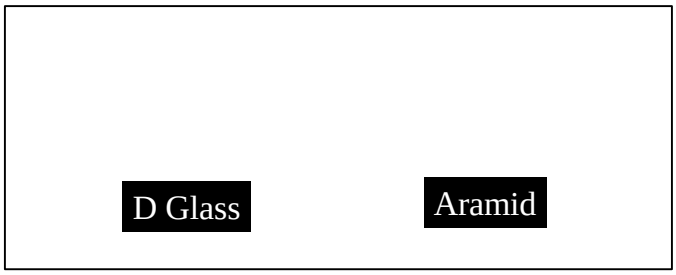

Figure 6: Microcracking experimentation: light polarized microscope

Calculations show residual shear stress at interface about 40MPa. This value is interesting since it is corresponding to the maximum value of IFSS measured by microbond pull out test near the gel point.

Moreover, a virtual interphase has been simulated at fiber matrix interface. Both interface thickness and Young modulus are investigated. Considering a 75 micrometers droplet diameter, 3 interphase thicknesses are studied (0.15, 0.5, 1 μm) as well as 3 Young moduli (3, 1 and 0.05 GPa). This rapid study shows that:

- Young modulus has more influence when thickness increase;
- The higher is Young modulus, the less influence has interphase thickness;
- The higher is Young modulus, the higher is shear stress at interface but until a limit.

One may conclude that even if there is no significant interaction between sizing and matrix, mechanical stress into matrix could lead to strong bonding between matrix and fiber and lead to cohesion in composite materials.

Processing effects: Application of dielectric spectroscopy.

Till now, discrete microdroplets were proceeded by direct deposition of a small amount of liquid resins onto fiber surface. As a consequence, resin becomes immediately solid through cooling. One could estimate a contact time between sizing and liquid resin near zero, leading to no significant interaction between sizing and matrix.

In order to estimate interaction during processing stage and in the same way to be closed to industrial process, different processing cycles have been studied:

Isothermal treatment at atmospheric pressure 100°C and 120°C;

Low pressure (27mm Hg) cycle at 100°C.

Those stages are applied to microdroplet before curing.

Firstly, different low pressure time preprocessing are investigated on IFSS. Results are compared to a reference sample microdroplet process under atmospheric pressure. After curing, IFSS increases versus preprocessing time as regard to the reference sample (*Figure 7*). Then, low pressure time is fixed and IFSS is studied versus conversion, compared to a reference (*Figure 8*). IFSS is 1,5 magnificated when low pressure process is applied, whatever conversion.

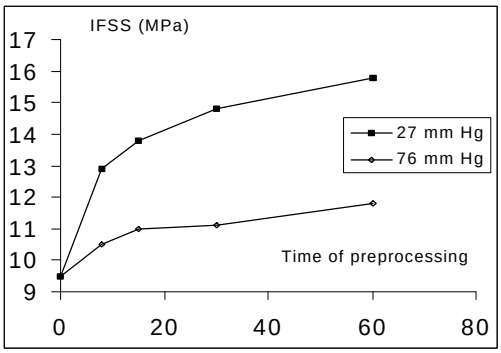

Figure 7: IFSS versus time of vacuum applied

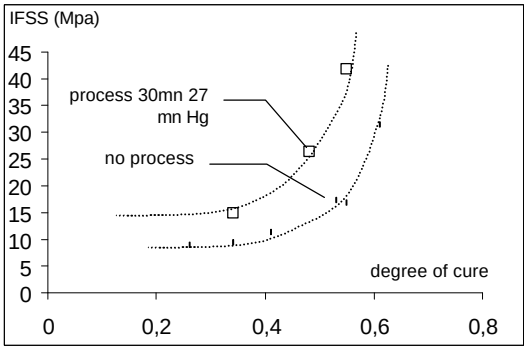

Figure 8: IFSS versus conversion under given preprocess conditions

Recent development in dielectric spectroscopy[8] show possibility to reach molecular interaction between matrix and sizing during processing. By measuring ionic conductivity(σ) of a sizing film wetted by a semi infinite matrix media, interpenetrating mechanisms are overlaid before cure stage. In other words, this approach can quantify whether strong interaction occurs between sizing and resin during process or not. Phenomenology of such a method is describe on *Figure 9*. Dielectric sensor are then coated with a sizing film. Authors report that a magnification of 3 relative to the equilibrium value is significant. During our trials at 100°C, no reliable evolution occur since ionic conductivity remains nearly constant (magnification of 1,2), as reported on *Figure 10*. When temperature process rises from 100°C to 120°C strong effect occur. As regard to Larson's tests, ionic conductivity shape leads us to conclude on sizing film dissolution into matrix media.

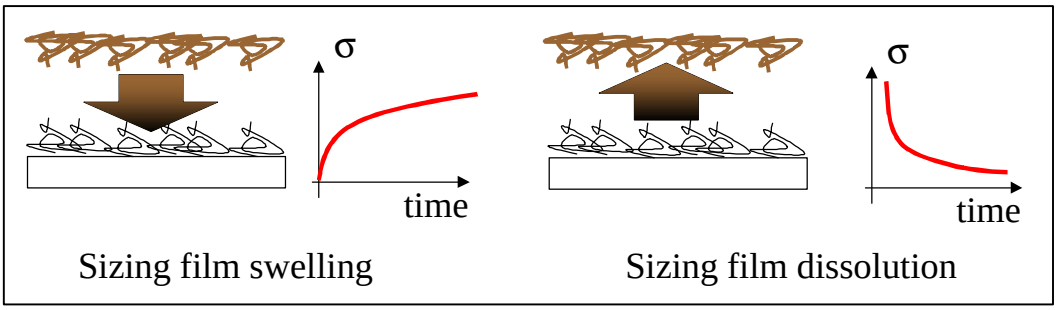

Figure 9: Dielectric method

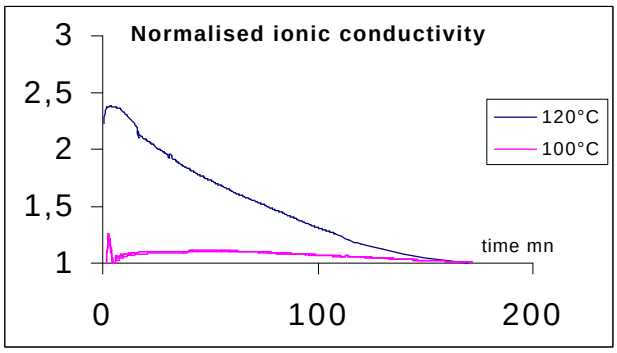

Figure 10: Dielectric measurement at 10Hz

Since it is not permitted to get live vacuum measurements with our technique, only discrete values of σ are recorded at given isothermal conditions. So, sample is first treated at 100°C for 20mn and then σ is measured. Value obtained is the highest measured of all process. Since σ is to be analyzed as an interpenetrating mechanism measurement tool, this could mean that matrix diffusion term is leading in case of vacuum process. In other words, vacuum process results in matrix diffusion into sizing film, whereas atmospheric process leads to sizing film dissolution into matrix media.

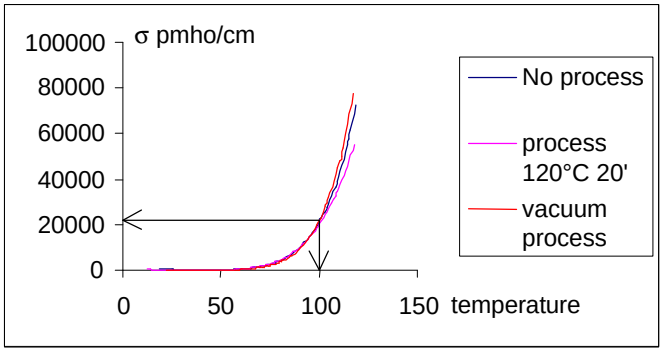

Figure 11: ionic conductivity versus temperature for different process (10Hz)

Then, to understand why no interaction occur at 100°C, *Figure 11* show evolution of ionic conductivity versus temperature for different process stages. No difference is noticed before 100°C. This means that before this temperature, matrix is not fluid enough to interact with sizing film. That's why, no interaction and no effect are noticed at atmospheric 100°C process.

Conclusion

A molecular interaction model is proposed to cross dielectric results with mechanical and numerical ones.

In case of vacuum process, matrix diffuse into sizing film. This leads to increase molecular concentration near interface. During resin curing, microgel could then develop directly into sizing film. This could increase Young modulus of interphase formed as regard to a sizing film one as a reference.

In case of atmospheric process, higher temperature leads to low resin viscosity as mentionned on *Figure 11*. Sizing film dissolute into matrix media. As a result, molecular concentration near interface decreases, whereas interphase thickness tends to increase. Interface Young modulus remains sizing one. Those analysis are closely related by numerical investigations. As mentioned previously, parts of shrinkage increase with increasing interphase Young modulus, or reducing interphase thickness.

In fact, in case of atmospheric process, interphase is made of bulk matrix and little sizing dissolute acting as anchors. In case of vacuum stage, interphase results from many anchors wetted by matrix.

According to Nardin and al[9] analysis of adhesion, IFSS is correlated to reversible work of adhesion (depending on the resin/sizing system) and to an average interfacial anchorage distance δ. In case of atmospheric process, proposed model assumes δ as the distance between each interacting sizing molecules, δ_1. In case of vacuum process, anchorage distance results from blending of resin and sizing. Microgel development into sizing film contribute to crosslinkage of sizing film itself. One could think that anchorage distance is not to be taken between wetted sizing molecule but between sizing molecule and microgel, so about $\delta_1/2$. IFSS measurement show a magnification of 1.5-1.7 between atmospheric and vacuum process.
This mechanism is summarized on *Figure 12*.

Figure 12: Interaction mechanism

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