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# VINYLESTER / GLASS FIBER INTERFACE : STILL A KEY COMPONENT FOR DESIGNING NEW STYRENE-FREE SMC COMPOSITE MATERIALS

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## ABSTRACT

Sheet moulding compounds (SMC) allow to design high performance polymer-matrix composites increasingly used for structural applications in the automotive industry. SMC are usually based on an unsaturated polyester thermosetting resin diluted in styrene with chopped glass fibers and fillers. Due to international regulations linked with the potential risks of styrene, replacing such styrene-based reactive system compound is becoming more and more strategic in order to zero-VOC emission, while keeping similar (or displaying even better) mechanical properties and shrinkage control to conventional SMC-based composite materials. In this study, the same sized E-glass fiber was combined with two different vinylester matrices, a conventional styrene containing resin and a styrene free one. The second type fits more suitable for friendly environmental purposes as it is based on a dimethacrylate diluent. The objective of this work is focused on interfacial adhesion in both systems as the fiber/matrix interface is a key parameter governing the mechanical properties of the final composite materials. A multiscale analysis was carried out from : *i*) the fiber scale by measuring the interfacial shear stress by using the microbonding test; *ii*) the fibers bundle scale by studying the wettability of fibers by the uncured resin; *iii*) up to the mechanical characterization of unidirectional SMC composites by measuring the interlaminar shear strength (ILSS). As main results, it is demonstrated that the styrene-free composites have a suitable interfacial resistance compared to conventional systems whereas impregnation, *i.e.* specific fiber sizings which will be more soluble in the resin-dimethacrylate reactive system need to be designed.

Keywords : Polymer matrix composites (A), Glass fiber(A), Fibre/matrix bond (B), Interfacial strength (B), multiscale modelling(C)

## INTRODUCTION

Fiber reinforced polymer (FRP) composites are widely used for a large range of structural and functional applications due to their superior performances, *i.e.* high strengths at break in various modes and stiffness, combined with their contribution to a weight reduction of the final composite parts. Sheet moulding compounds (SMC) have received an increasing attention according to their high strength-to-weight properties as engineering materials in automotive industry in the recent decades [1-3]. These thermoset-based composite materials usually consist of unsaturated polyester oligomers diluted in styrene monomer, magnesium oxide as thickening agent, glass fibers, and calcium carbonate fillers. Usually, the polyester resins contain 35-50 volume percent styrene monomer. Nevertheless, styrene monomer is classified as a potential carcinogenic and neurotoxic agent as well as a respiratory

tract irritant which can lead to health hazards for workers who are exposed to either vapors or direct contacts. The styrene monomer plays a dual role as it allows to dilute the prepolymer and to tune the resin viscosity and copolymerize with UP prepolymer during SMC curing process. However, because of its very low olfactory threshold of styrene, 0.32 ppm, at the initial stage of the uncured resin and/or as remaining monomer in the cured SMC parts, new alternatives to use of styrene are required. Nowadays, new routes are developed for SMC formulations in order to enhance the mechanical performances of the resulting composites. These approaches consist of substituting the conventional polyester resins by a vinylester-based one or introducing block copolymers [4]. Vinylester prepolymers could be preferred owing to their thermomechanical behavior similar to epoxy-based thermosets while showing the same curing range as polyesters ones. Biosourced prepolymers are also under investigation [5, 6].

The aim of this study is to reduce and replace styrene monomer combined with polyester resins with alternative monomers that are known to be less hazardous. The alternative monomers are selected based on their reduced risk for health, their low cost, and their low viscosity and of course their ability to copolymerize with the polyester prepolymers. Several potential bio-based methacrylate derivatives, namely, butanediol dimethacrylate (BDDMA), isobornyl methacrylate (IBOMA), and lauryl methacrylate (LMA) were considered as alternatives to styrene as reactive diluent of unsaturated polyesters (UPR). In a first part of the study, the ability of these compounds to fit with the SMC process steps has been studied in terms of volatility, miscibility with UPR, and viscosity of the resulting reactive resin. Based on these preliminary studies, butanediol dimethacrylate (BDDMA) was selected as reactive diluent [7].

Nevertheless, the performances of the SMC-based composite materials remain dependent on the interfaces between material components and in particular fiber-matrix interface or the interphase region that ensures the stress transfert from the matrix to the fiber [8, 9]. E-glass fibers used for SMC are made of bundles assembling thousands of yarns of individual fibers having a diameter of about 15  $\mu\text{m}$ . The fiber ability to be wet by the resin during the impregnation step, before and after maturation step, as well as after molding and curing is a critical parameter in order to avoid void formation and heterogeneous spreading of the resin outside the bundles (wet-out) but also inside the bundles (wet-through). However, wetting is a required condition but not the only one parameter that has to be taken into account. In fact, the final interfacial adhesion needs to be as high as possible as the matrix-to-fiber stress transfer governs the mechanical properties such as toughness and failure mode of the resulting SMC composites.

As the SMC formulation is a complex medium, the effect of each component must be distinguished in order to have a better understanding of the role of each one. Thus, the aim of this study was to develop a multi-scale and multi-step approach that will allow the characterization of the wetting and the impregnation of the glass fiber surface by the matrix and the characterization of the interfacial adhesion between the cured polymer matrix and the E-glass fiber, *i*) at micro-scale using a microdebonding to determine interfacial shear strength (IFSS) and *ii*) at the macro- scale considering unidirectional SMC composites to determine interlaminar shear strength (ILSS). As styrene monomer is substituted by a methacrylate reactive diluent in order to achieve a lower VOC emission and a reduction of olfactory effects, the styrene-free composite must keep similar mechanical properties and shrinkage control to conventional SMC composite materials. Therefore, the effect of such a diluent on the interfacial properties was investigated from the comparison between two types of interfaces based on the same E-glass fiber: *i*) a reference model based on a mixture of unsaturated polyester and vinylester diluted in styrene as matrix and *ii*) an innovative matrix based on a styrene-free vinylester matrix.

## EXPERIMENTAL

### Material and Methods

A commercial E-glass roving from Owens Corning was used and the properties of the E-glass filaments are listed in Table 1. The non-soluble and soluble fractions in styrene monomer of the fiber sizing corresponding respectively to the grafted part and the physically adsorbed part were measured by thermogravimetry analysis.

Two different Sheet Molding Compound (SMC) composite formulations were investigated based on diglycidyl ether of bisphenol A vinylester resin, one with styrene (noted Resin A) and the second one free-styrene (noted Resin B). Resin A is a blend of vinylester and maleated unsaturated polyester whereas the Resin B is only made of vinylester. Reactive diluent for Resin B is 1,4-butanediol dimethacrylate (BDDMA) as an alternative to styrene [7]. The chemical structure of components is reported in Figure 1 and the characteristics of matrices are given in Table 2. Unlike styrene, BDDMA is tetrafunctional with methacrylate end groups like vinylester ones. If vinylester and styrene tend to copolymerize, BDDMA tends to homopolymerize leading to a random copolymer with a high ratio of BDDMA. The higher viscosity of styrene free matrix justifies the more important ratio of reactive diluent (60% of BDDMA against 30% of styrene). But the excellent thermal stability of BDDMA gives it a serious advantage in comparison with styrene.

The SMC resin paste usually used for SMC composites materials have the following composition (in wt %): Vinylester in reactive diluent 18.7, low profile additive in reactive diluent 4.7, catalyst 0.4, calcium carbonate (CaCO<sub>3</sub>) 23.3, release agent 1.4, magnesia 1.6 and glass fibers 50.0. Nevertheless, for understanding the fiber/matrix interactions and their consequences on the mechanical properties of multi-fibers composites, unidirectional (UD) composites were molded from formulations without CaCO<sub>3</sub>.

Table 1 – E-glass fiber characteristics

| Nature of glass | Tex (strand) | Fiber diameter (μm) | Sizing (%wt) | Styrene-soluble part of the sizing (%wt) | Nature of the film former  |
|-----------------|--------------|---------------------|--------------|--|--|
| E-glass         | 2,200        | 15                  | 1.86 ± 0.20  | 0.84 ± 0.08                              | Polyvinylacetate (PVAc)<br>(Unsaturated polyester & vinylester-compatible) |

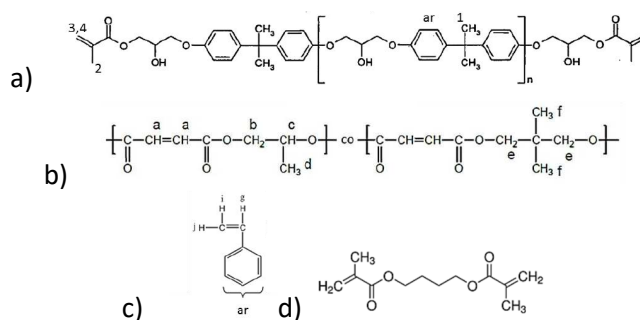


Figure 1-Chemical structures of the various types of resin used as matrices: (a) vinylester; (b) unsaturated polyester and reactive diluent comonomers: (c) styrene; (d) butanediol dimethacrylate BDDMA

Table 2 – Polyester/vinylester and vinylester matrices characteristics

| Matrix | Mn <sup>a</sup> (g.mol <sup>-1</sup> ) | Vinylester content <sup>b</sup> (wt%) | Polyester content <sup>b</sup> (wt%) | Reactive diluent content <sup>c</sup> (wt%) | Viscosity@20 °C (mPa.s) |
|--------|--|---------------------------------------|--------------------------------------|---|-------------------------|
| A      | 1,250                                  | 48                                    | 52                                   | 35 (styrene)                                | 1,000                   |
| B      | 2,900                                  | 100                                   | 0                                    | 60 (BDDMA)                                  | 2,500                   |

<sup>a</sup>The average molar mass by number was determined by size exclusion chromatography using polystyrene standards

<sup>b</sup>The ratio vinyl ester-to-polyester was determined by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz)

<sup>c</sup>The final reactive diluent content was determined by thermogravimetric analysis (heating ramp: 10 K.min<sup>-1</sup>)

### Curing and processing conditions

For micromechanical tests, matrices A and B were cured using 1 phr of methyl ethyl ketone peroxide (MEKP) as initiator and 0.02 phr of cobalt octoate as accelerator. The cure schedule was 24h at room temperature, 4h at 80°C, 4h at 120°C, and 4h at 180°C. This gradual curing was chosen in order to avoid the loss of the reactive diluent, *i.e.* styrene or BDDMA. Differential Scanning Calorimetry (DSC) and Dynamical Mechanical Spectroscopy (DMS) confirmed that the reaction was therefore completed after the selected cure schedule.

Unidirectional SMC composites were from 5 initial layers with dimensions of 120 x 250 mm<sup>2</sup> and molded at 145°C for 180s under 20 bars. After molding, the thickness of the composites was close to 3 mm.

### Dynamic Mechanical Spectroscopy (DMS)

DMS was used to determine the dynamical mechanical properties, *i.e.* the storage, E', and loss, E'', moduli and the loss factor, tan δ. The temperature at the maximum of tan δ is associated to the glass transition temperature of the vinyl ester network. A DMS TA ARES II instrument was used in 3-points bending mode. The heating rate was 3 K.min<sup>-1</sup> and the frequency was 1Hz.

### Wettability analyses

In order to evaluate the wettability of the fiber by the two reactive systems selected as matrices, wetting measurements were performed. For performing surface energy measurements on the glass fiber filaments, an Apollo Instruments DCAT 21 tensiometer was used as a Wilhelmy balance. Glass fibers were fixed onto a holder by means of an adhesive tape. Four filaments were considered in order to increase the signal-to-noise ratio. Three different probe liquids were used : water, methylene diiodide, and ethylene glycol. 10 samples were used for each probe liquid. The contact angle determinations with probe liquids allow to calculate the total fiber surface energy, γ<sub>S</sub><sup>T</sup>, and its dispersive, γ<sub>S</sub><sup>D</sup>, and non-dispersive, γ<sub>S</sub><sup>ND</sup>, components by using the Owens-Wendt approach [10] (Eq (1)).

$$\frac{\gamma_L \cos(\theta + 1)}{2(\gamma_L^D)^{1/2}} = (\gamma_S^{ND})^{1/2} \frac{(\gamma_L^{ND})^{1/2}}{(\gamma_L^D)^{1/2}} + (\gamma_S^D)^{1/2} \quad (1)$$

where γ<sub>L</sub> is the surface energy of the probe liquid and its dispersive, γ<sub>S</sub><sup>D</sup>, and non-dispersive, γ<sub>S</sub><sup>ND</sup>, components.

The surface energy of the thickened SMC paste, *i.e.* before molding, was determined using an Apollo Instruments Digidrop and from the contact angle of a probe liquid droplet on the SMC flat surface. The probe liquids considered were water and methylene diiodide. The surface energy was also determined by the Owens-Wendt' equation (Eq (1)). The wettability of the sized E-glass fibers by the SMC paste could therefore be evaluated by comparing surface energies and considering the Zisman criterion [11].

The wettability measurements were also performed using a Zeiss optical microscope from the observation of the shape of microdroplet deposited on E-glass filaments having a diameter, df, equal to 15 μm. Thus, the wettability could then be evaluated by measuring the contact angle between the filament and the droplet and the aspect ratio Le/d, as shown in Figure 2, where Le is the embedded length and d is the diameter of the microdroplet. These measurements were done before and after curing leading to the determination of the spreading coefficient, denoted S (Eq (3)) [12], and of the work of adhesion W<sub>SL</sub> (Eq (4)) from the Young-Dupré' equation (Eq (2)).

$$\cos \theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad (2)$$

$$S = \gamma_S - (\gamma_{SL} + \gamma_L) \quad (3)$$

$$W_{SL} = \gamma_L(1 + \cos \theta) \quad (4)$$

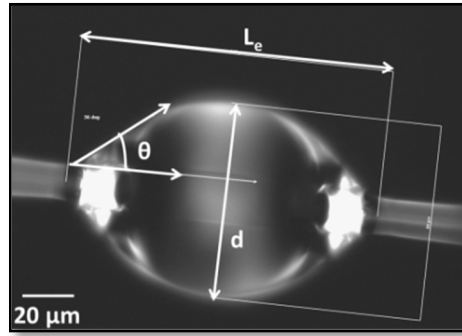


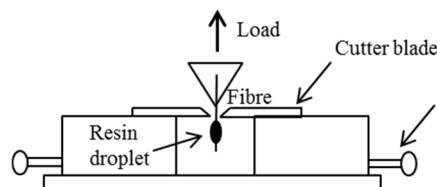
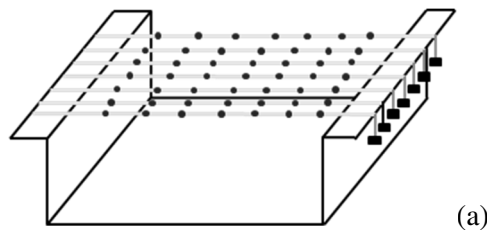
Figure 2- Vinylester microdroplet deposited on a E-glass filament

### Microtomography

X-ray microtomography measurements were performed using laboratory X-ray source on an easytom tomograph from RX Solutions Co. Data recording was done using a polychromatic source operated at 100 kV and a voxel lateral isotropic size of 0.3 mm.

### Interfacial shear strength, IFSS, from microdebonding

Individual fibers were glued onto a metal frame and droplets of resin were deposited using a copper filament. The entire assembly (Fig.3) was then transferred into an oven for curing. The cure schedule was the one reported previously. Until reaching the gelation time, the atmosphere was saturated with styrene in a closed box in order to avoid styrene evaporation from the microdroplets. After curing and cooling down to room temperature, the samples were prepared from symmetric droplets and the filaments were glued onto triangular paper holders which were mounted in a tensile machine with 10 N load cell. Embedded length, droplet diameter, contact angle, and fiber diameter were measured using an optical microscope in order to calculate the interfacial shear strength, denoted IFSS, and to characterize the wettability after curing.



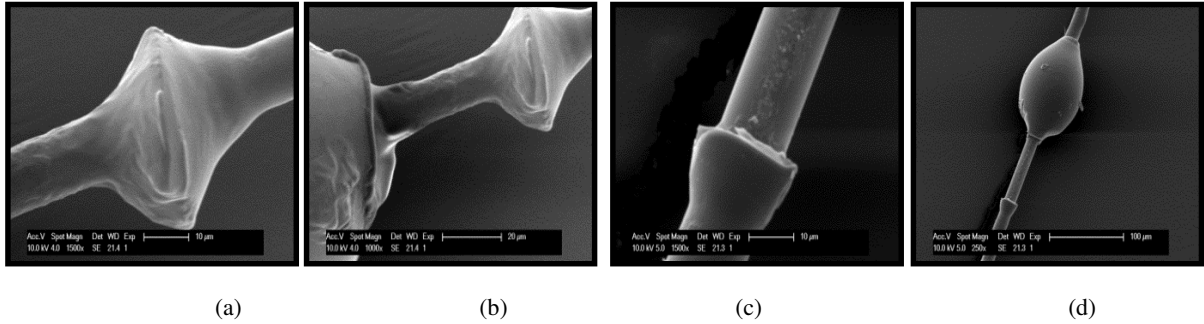
(b)

**Figure 3 - Microdebonding test: (a) Preparation of microdroplets on individual fibers ; (b) Debonding**

The device used to perform microdebonding was made from two cutter blades mounted on a movable test bed controlled with micrometer screws (Fig.3). A camera was used to help positioning the cutter blades and to monitor the test. The displacement rate was  $0.1 \text{ mm.min}^{-1}$ . The fiber was pulled-out as the microdroplet is blocked by the two blades and the load-displacement was recorded until debonding occurred. The maximum force at debonding,  $F_{\max}$ , was considered together with the interfacial area in order to calculate the average interfacial shear strength, IFSS, as calculated from Eq. (5) *i.e.* considering a constant shear stress along the embedded length [13]. 20 to 30 single tests were performed for each fiber/matrix combination. The debonding zone was observed by optical (OM) and scanning electron (SEM) microscopies (SEM) to verify the validity of the test. Examples of debonded microdroplets are shown in Fig.4.

$$\tau = \frac{F_{\max}}{\pi L_e d_f} \quad (5)$$

where  $F_{\max}$  is the maximum force,  $L_e$  is the embedded length and  $d_f$  is the glass filament diameter.



**Figure 4 - SEM micrographs of different debonded microdroplets (Matrix A): (a,b) cohesive failure of the matrix; (c,d) adhesive failure of the fiber/matrix interface.**

### **Interlaminar shear strength, ILSS, from short-beam shear test**

The unidirectional SMC E-glass fiber/vinylester composites were tested using the short-beam shear test. The bending beam specimens were cut directly from the composite plate. The dimensions were chosen in order to enhance shear stress in the neutral fiber plane (*vs.* tension/compression modes on the external planes), *i.e.* for promoting shear failure. Thus the length-to-sample thickness ratio, denoted as  $\lambda$ , was set below 5 and the displacement rate for the 3-points bending test was  $1 \text{ mm.min}^{-1}$  [14]. The load-displacement was recorded for each test until failure and the maximum force at interlaminar fracture,  $F_{\max}$ , was used in order to determine the interlaminar shear strength, ILSS, as shown in Eq. (6).

$$\text{ILSS} = \frac{3F_{\max}}{4bt} \quad (6)$$

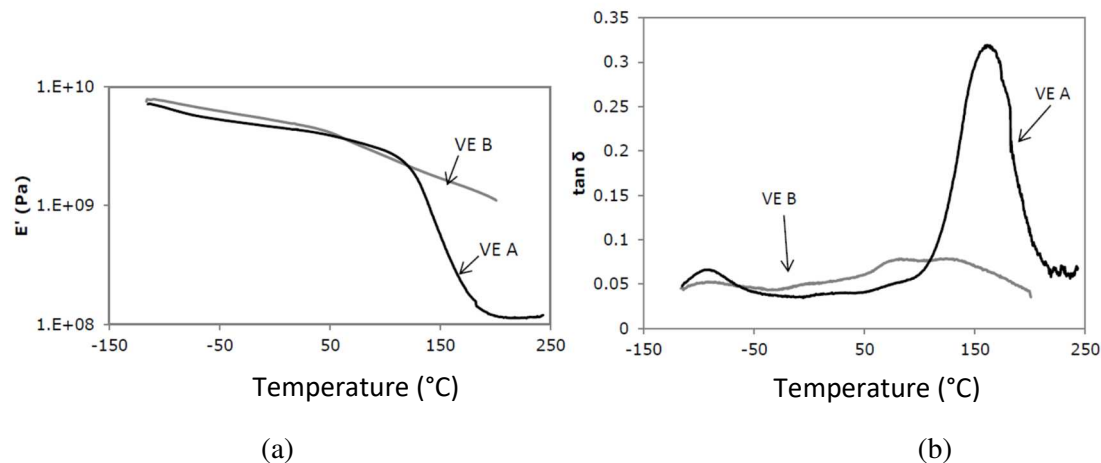
where  $b$  and  $t$  are the thickness and width of the sample, respectively.

ILSS which characterizes interlaminar shear strength determined at macroscale was compared to IFSS values determined at micro-scale for the different fiber/matrix combinations considered for SMC composites.

## RESULTS AND DISCUSSION

### 1. Thermomechanical behavior of vinylester networks

The storage modulus,  $E'$ , and the loss tangent,  $\tan \delta$ , as a function of the temperature of the neat vinylester networks after curing are given in Fig. 5. The temperature of the main mechanical relaxation,  $\alpha$ , which is related to the glass transition of the matrix A, *i.e.* with styrene-monomer as reactive diluent, occurs close to 155°C. This network looks to be relatively homogeneous in terms of crosslinking topology according to the broadness of the  $\tan \delta$   $\alpha$ -peak even though the free radical polymerization mechanism is known to lead to heterogeneous networks compared to the ones resulting from polyaddition. For styrene-free matrix B, the loss tangent peak has a very low amplitude and a very large broadness. As a consequence, the storage modulus in the rubbery region remains very high compared to the styrene-based network. This means that the crosslink density of this network is high, *i.e.* the average molar mass between crosslinks is very low. It can be explained by the fact that in both cases, the reactive diluents could homopolymerize but as in the first case, styrene leads to polystyrene chains, whereas BDDMA homopolymerizes as a dense network due to the functionality of this dimethacrylate compound, *i.e.* 4.



**Figure 5 – DMS spectra recorded at 1 Hz of the network A (styrene-based) and the network B (BDDMA-based):**

**(a) storage modulus,  $E'$  and (b) loss tangent  $\tan \delta$  as a function of temperature**

A good wetting at the initial stage, *i.e.* before curing, is required in order to achieve an intimate interfacial contact between the fiber and the matrix. For SMC composite materials, the impregnation step (wet-through and viscosity depending) during calendaring is another key step that also determines the final properties of the composite. Nevertheless, a perfect wetting is the first condition to build the fiber/matrix interface which is characterized by the thermodynamic work of adhesion.



### 2.1. Surface energy of individual components

To assess the wettability of fiber by the vinylester resin, the surface energy of both components must be determined. The surface energy and its dispersive and non dispersive components obtained according to the previously described protocol are given in Figure 6. The sized E-glass fiber shows mainly a dispersive character even if the non-dispersive component close to  $17 \text{ mN.m}^{-1}$  is high. These results are quite similar to those reported in the literature ones [15,16]. The surface energy of the fiber is higher than the one of neat PVAc ( $36.8 \text{ mN.m}^{-1}$ ) used as film former in the sizing [17]. This can be explained by the complex nature of the sizing covering the fiber surface that includes the condensed and non-fully condensed organosilanes, emulsifier(s), and additives contributing to the non dispersive component of the surface energy of the fiber [18]. In order to evaluate the wettability of the glass fibers towards the SMC matrix, the empirical Zisman's wetting criterion can be considered, *i.e.* the fiber surface can be wet by the SMC vinylester resin if the fiber surface energy is higher than the later one. The wettability criterion should be refined by taking into account the dispersive and non-dispersive components of the fibers. If these ones are close to SMC resin ones, suitable interactions are expected to take place and to improve the wettability. Based on the results shown in Figure 6, it can be concluded that the fibers will be easily wet by the vinylester resin. The substitution of styrene by BDDMA leads to an increase of dispersive component and a strong decrease of non dispersive component. Thus, the wettability is expected be better for the conventional styrene-based resin compared to the dimethacrylate-based resin This phenomenon is related to the fully dispersive character of the styrene-free resin (BDDMA-based), while the sized glass fiber surface displays a highly polar character which is quite close to one of styrene-based resin (matrix A).

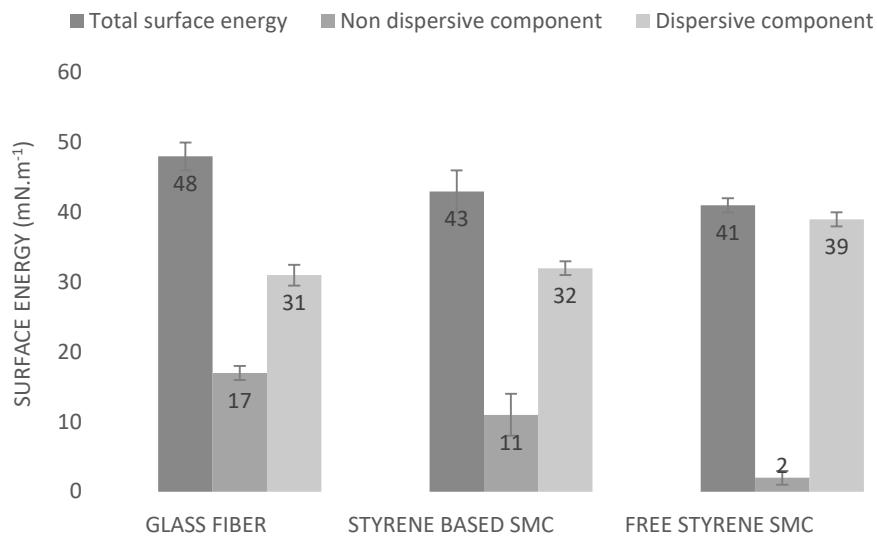
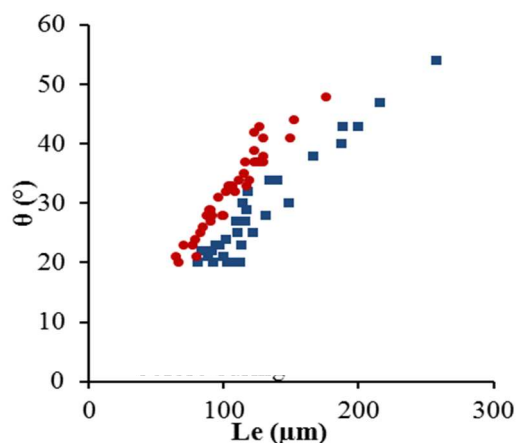


Figure 6 - Surface energies of E-glass fiber and SMC resins (before curing)

### 2.2 Wettability of fiber by vinylester resin

Figure 7 reports the contact angles obtained before curing for microdroplets formed by non-polymerized vinylester resins on glass filaments. Nevertheless, a direct measurement of contact angles cannot be done directly due to the cylindrical shape and the small diameter of the fiber in contrary with planar surface geometry. Thus, a linear increase of the contact angle with the embedded length is obtained [14,19-20]. While keeping in mind that the observed contact angle is not the absolute one, these values can still be used in order to compare the wettability of the sized E-glass fibers with the two types of vinylester resins.



**Figure 7 - Dependence of the contact angle formed by the uncured resins (styrene-based resin A (blue squares) and BDDMA-based resin B (red circles)) on sized E-glass fibers with the embedded length**

Averaged contact angles are reported for an embedded length of 100  $\mu\text{m}$  in Table 3. Whatever  $L_e$ , it can be concluded that the styrene-free resin, based on a dimethacrylate reactive diluent, has a lower ability to wet the glass fiber than the conventional one, based on styrene-monomer. This result is confirmed by considering the spreading coefficient,  $S$ , obtained from the surface energies of both components (Table 3).

**Table 3 – Comparison of contact angles for similar wet length,  $L_e$ , and/or aspect ratio,  $L_e/d$ , of microdroplets formed on E-glass fiber by the two types of uncured resins**

|                              | Embedded length ( $\mu\text{m}$ ) | Observed contact angle $\theta$ ( $^\circ$ ) | $L_e/d$       | $W_{SL}$ ( $\text{mN.m}^{-1}$ ) | $S$ ( $\text{mN.m}^{-1}$ ) |
|------------------------------|-----------------------------------|--|---------------|---------------------------------|----------------------------|
| <b>Styrene based Resin A</b> | $103 \pm 12$                      | $23.7 \pm 3.6$                               | $2.0 \pm 0.2$ | 72                              | -3.2                       |
| <b>Free styrene Resin B</b>  | $102 \pm 14$                      | $31.1 \pm 4.8$                               | $1.7 \pm 0.2$ | 65                              | -7.7                       |

The spreading parameter  $S$  is in both cases negative meaning that the wetting is partial which is in agreement with previous observations. However, these results confirm that the wetting is better for a styrene-based vinyl ester resin, *i.e.* lower contact angle, higher  $L_e/d$  and work of adhesion. These considerations do not take into account the additional interactions which can occur at the interface such as the dissolution and/or swelling of the sizing by the vinyl ester resin during impregnation and curing steps. Thus, the dissolution of the fiber sizing into the reactive diluent, styrene-monomer or BDDMA dimethacrylate, was studied.

### 3. Sizing solubility in reactive diluent

In the presence of a sizing, the good wetting of the fiber with the resin means that the sizing must be swollen by the components of the reactive vinyl ester system and/or partially soluble in the reactive diluent. The calculation of solubility parameters allows to assess the sizing solubility in the two different reactive diluents. It is known that the glass fiber sizing is mainly composed of a film former, in this case PVAc, and coupling agents, organosilanes. The condensed coupling agents are chemically bonded to the glass fiber surface and cannot be extracted. Therefore, only the film former, can be soluble in the reactive diluent. Thus, it is possible to predict the interaction parameter,  $\chi$ , between

PVAc and the reactive diluents from the solubility parameters. The solubility parameters reported in Table 4 are calculated from the group contribution method [21-22].

$$\chi = \frac{V}{RT} (\delta_P - \delta_S)^2 \quad (7)$$

where P is the polymer, S the reactive solvent, V the molar volume, R the universal gas constant, and T the temperature.

**Table 4 - Solubility parameters of styrene, BDDMA and PVAc by using Hansen's table and Van Krevelen theory**

| Component | $\delta$ (J <sup>1/2</sup> .cm <sup>-3/2</sup> ) |
|-----------|--|
| Styrene   | 18.8   |
| BDDMA     | 16.1   |
| PVAc      | 20.7   |

An interaction parameter below 0.5 means good miscibility of polymer in the solvent. The results presented in Table 5 show that, compared styrene or acetone, BDDMA is not a good solvent of the film former (PVAc) on the glass fiber. This lack of miscibility confirms the lower wettability of glass fibers by the styrene-free resin compared to resin A based on styrene monomer as reactive solvent.

**Table 5 – Interaction parameter of PVAc with various solvents**

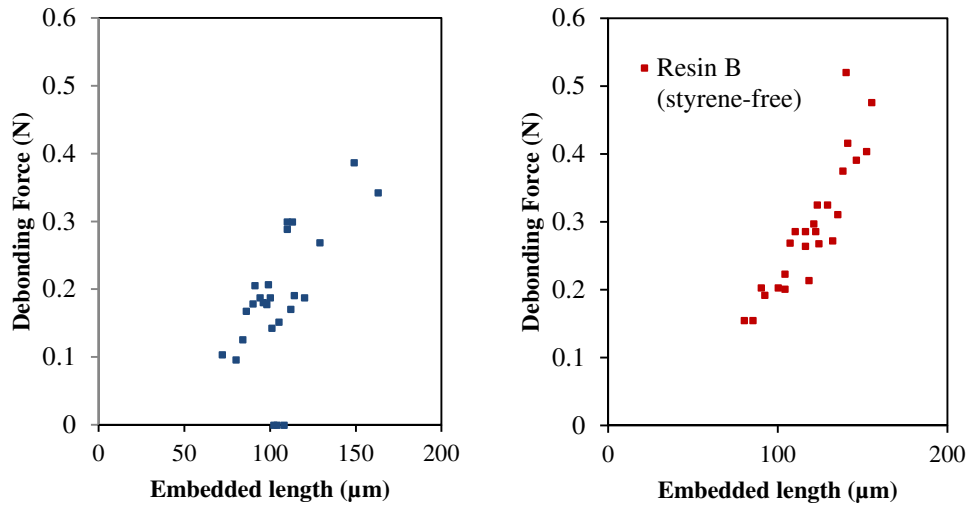
| Combination  | $\chi$ |
|--------------|--------|
| PVAc-Styrene | 0.14   |
| PVAc-BDDMA   | 1.90   |
| PVAc-Acetone | 0.06   |

#### 4. Micromechanical analysis of the E-glass fiber/vinylester interfaces

In order to analyze the interfacial adhesion from the microbonding test, the average IFSS (interfacial shear strength from a Kelly-Tyson' model) was calculated according to Eq (5). This simple approach allows a direct comparison between fiber/matrix interfaces. Due to the high level of interfacial adhesion between the glass fiber and the thermoset matrix, the microdebonding test cannot be performed when embedded lengths are higher than 200  $\mu\text{m}$  in both cases. In fact, for long embedded lengths, fiber breaks in the free length, *i.e.* in the free length between the matrix droplet and the fiber clamping. Figure 10 represents the debonding force as a function of embedded length for the two types of vinylester resins. The scattering of the data are inherent to this kind of test which are dependent on many experimental parameters [23]. It should be mentioned that Greszczuk's stress criterion model [24] and Penn & Lee's energy model [25-26] were also considered to analyze these micromechanical data. Unfortunately, due to the linear increase of the debonding force with the embedded length, it was not possible to fit the experimental data. This can be explained by the very narrow range of embedded length which can be considered to perform the microdebonding test (from 70 to 180  $\mu\text{m}$ ), due to the existence of a very strong interface established from covalent bonding between the sized E-glass surface and the matrix.

As shown in Figure 8, the interfacial properties seem similar as the debonding force linearly increases with the embedded length according to a same dependence. As a consequence, the calculated average interfacial shear strengths of the interfaces are very close (Table 6). The relatively high

standard deviations highlight the significant number of trials must be required to take into account the random character inherent to the microbonding test.



**Figure 8 - Debonding force as a function of embedded length for vinyl ester matrix A / glass fiber (left) and styrene-free vinyl ester matrix B / glass fiber interfaces (right)**

The styrene-free vinyl ester matrix (matrix B) displays a slightly higher interfacial shear strength whereas a better wettability with the styrene-based vinyl ester matrix (matrix A) is observed. This result demonstrates that the wettability criterion is initially required but is not sufficient to ensure a high interfacial adhesion after curing.

As the Kelly-Tyson’ model supposes a constant stress along the embedded length, IFSS could be compared to the shear yield stress,  $\tau_Y$ , of the matrix. The compression yield stress for the vinyl ester matrix is close to 100-130 MPa which leads, according to a Von Mises’ criterion, to a shear yield stress equal to 90 MPa [27-28]. As expected, the IFSS does not exceed the shear yield stress of the vinyl ester matrix which means that the matrix didn’t undergo shear yielding for interface debonding .

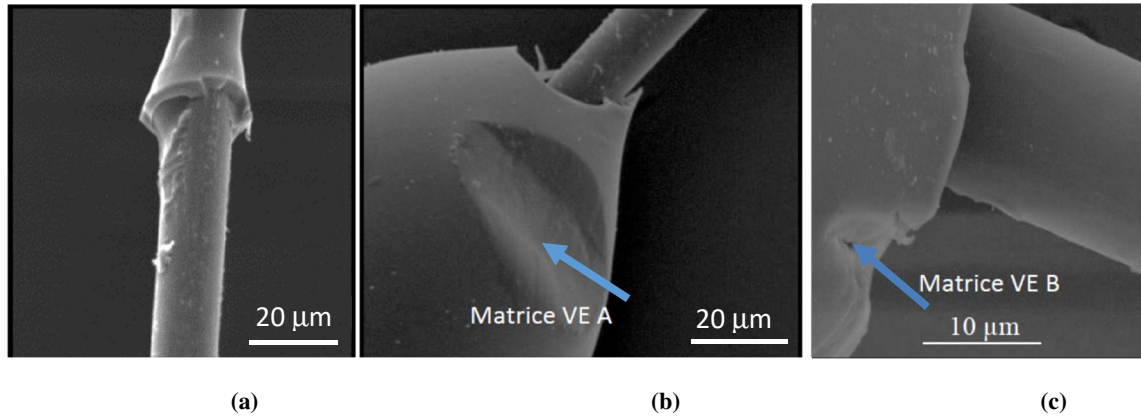
**Table 6 – IFSS for the two matrices**

|                  | Matrix A                   | Matrix B   |
|------------------|----------------------------|------------|
| Prepolymer       | Vinylester/Polyester blend | Vinylester |
| Reactive Diluent | Styrene                    | BDDMA      |
| IFSS (MPa)       | 43±9                       | 49±11      |

**Determination of different types of**

The SEM pictures of debonded microdroplets (Figure 9) show a similar fracture mode in both matrices as described in literature [29]. The fracture initiation takes place when the pull out strength is the highest one as the fiber merges from the matrix in a Mode-I failure process perpendicular to the fiber axis (as evidenced by the presence of a residual meniscus of resin) before failure propagation in a Mode-II along the interface. The ability of both matrices to plastically deform in compression under the cutter blades used to clamp the droplet is shown with the help of arrows in Figure 9. Even if this phenomenon is common for thermoplastic matrices, this phenomenon was also observed for epoxy matrix/E-glass fiber interfaces. Thus, the IFSS was only characterized using the Kelly-Tyson’s model

and not energy-based models [30]. With such models, the interface toughness would be over-estimated due to energy consumption in plastic deformation under the blades.



**Figure 9 - SEM micrographs after microdroplet debonding of (a) the top part of the microdroplet (remaining meniscus), (b) the indented microdroplet by compression by the clamping blades, and (c) the clean fiber surface indicating an adhesive failure of the interface (whatever the nature of the resin)**

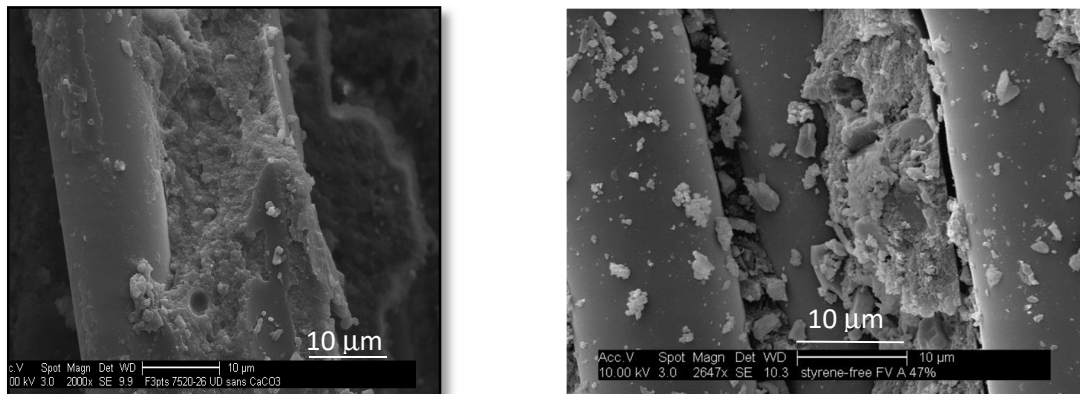
### 5. Unidirectional SMC composite materials

Micromechanical studies only make sense if the conclusions could be confirmed at the macroscale, *i.e.* on multiyarn composite materials. Indeed, the size and the geometry of the microcomposites put the micromechanical analysis in conditions far from the reality of multifiber composite materials. In fact, curing schedules seen by the resin are different, the state of internal stresses generated are not similar, the overlapping of the stress fields between surrounding fibers in the real composite is not taken into account in the single fiber microdroplet geometry, etc. That's why unidirectional SMC composites have been prepared in order to analyze the interfacial properties at the macroscopic scale using a dedicated tests enhancing the interface response, *i.e.* determination of interlaminar shear strength, ILSS, from 3-points bending test (Table 7).

**Table 7 - Unidirectional SMC composite materials properties**

| Sample       | Shrinkage (%) | C=C conversion (%) | Density (cm <sup>3</sup> .g <sup>-1</sup> ) | Glass fiber (wt%) | Glass fiber (vol%) | 3-point bending (L/D =5) |                              |                     |
|--------------|---------------|--------------------|---|-------------------|--------------------|--------------------------|------------------------------|---------------------|
|              |               |                    |   |                   |                    | Modulus (GPa)            | Flexural strength ILSS (MPa) | Strain at break (%) |
| GF / Resin A | 0.11          | 95.5               | 1.6   | 53.8 ± 0.2        | 33.0               | 26 ± 1                   | 800 ± 35                     | 3.4 ± 0.2           |
| GF / Resin B | 0.08          | 96.5               | 1.6   | 51.3 ± 0.7        | 30.2               | 25 ± 2                   | 657 ± 76                     | 2.9 ± 0.2           |

As the volume fractions of E-glass fibers in the two types of UD composites are similar, the mechanical properties can be compared. The interlaminar shear strength appears as a discriminant parameter for evaluating the stress transfer at the interface between the E-glass fiber and the styrene-based vinylester matrix A or styrene-free vinylester matrix B . Whereas at microscale, the interfacial shear strength, IFSS, was found to be slightly higher or similar for the BDDMA-based vinylester resin, conclusions issued from ILSS determined on UD composites are not the same. In fact, the stress transfer between matrix and fiber is not improved when the styrene-free matrix B is considered. However, the present observations made on the fractured surfaces reported in Figure 10 link with wettability analyses. This phenomenon could also be associated to the styrene evaporation occurring at microscale due to the large surface-to-volume ratio for microdroplets, leading to an underestimation of the IFSS values for styrene-based matrix A.



(a) (b)

Figure 10 - Fracture surface of UD composites based on E- glass fiber and (a) styrene-based vinyl ester matrix A and (b) BDDMA-based vinyl ester matrix B after ILSS 3-points bending test

### 6. Hydrothermal aging of the interfaces

The interface stress transfer level needs to be ensured after an hydrothermal aging, *i.e.* after humidity (95 RH%) and temperature (70°C) exposure. In fact, the water may diffuse at the interface leading to a poor stress transfer level which will contribute to deteriorate the mechanical behavior of the composite materials. An hydrothermal aging applied to microcomposites such as microdroplet is an efficient method to analyse the effect of aging on the interfacial shear strength owing to the high surface-to-volume ratio of the specimens, *i.e.* the time of exposure to water could be drastically reduced [31]. The IFSS values after exposure in different conditions are reported in Figure 11.

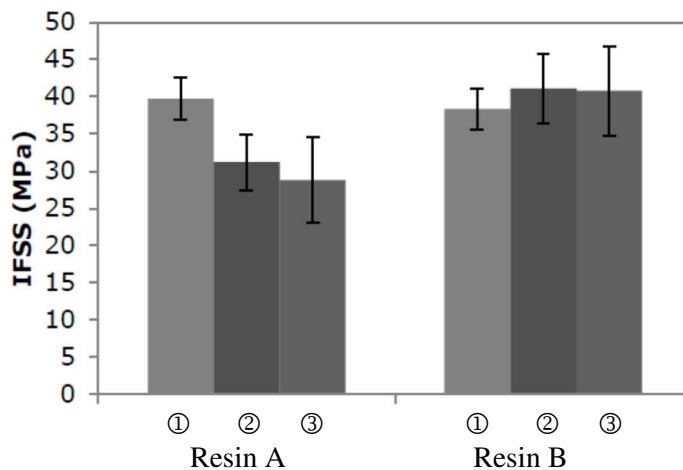
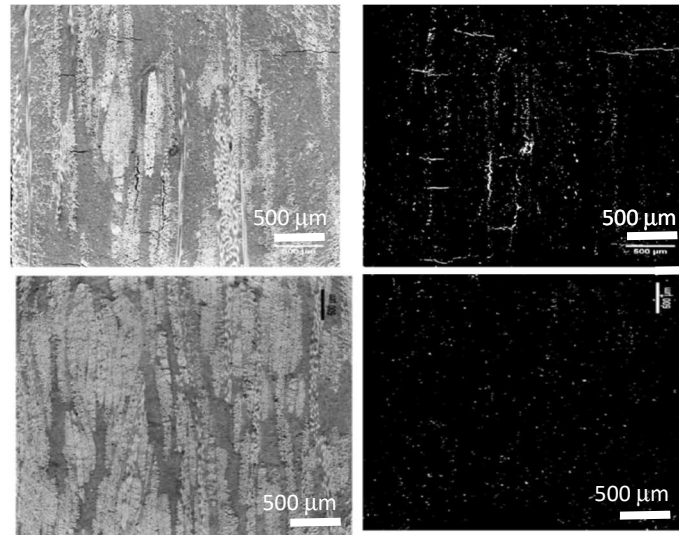


Figure 11 – Evolution of IFSS after hydrothermal aging for the interfaces between E-glass fiber and the two types of vinyl ester matrices

① : Dry    ② : 7 days @70°C, 95RH%    ③ : 14 days @70°C, 95RH%

A loss of 22% of IFSS is observed for the interface from glass fiber and styrene-based vinyl ester matrix highlighting the sensitivity of this type of interface to the hydrothermal aging. This loss can be associated to the presence of unsaturated polyester in the initial reactive resin which is more sensitive to the ester bonds hydrolysis. On the opposite, the aging has almost no influence on the interfacial shear strength as the BDDMA-based resin is considered. This phenomenon could be related to the fact

that pure vinylester matrix, *i.e.* without polyester prepolymers, is used. However, at the unidirectional composite scale, many cracks and porosities highlighted on X-rays tomography micrographs after thresholding appear after aging on the composites made from BDDMA-based matrix (Figure 12). These defects could occur from the hydrolysis of the BDDMA methacrylate reactive solvent. In comparison, no cracks are observed in the composite processed with styrene-based matrix which contains polyester.



**Figure 12 – X-Rays tomography micrographs after hydrolytic aging (7 days @70°C and 95RH%) of a unidirectional composite made from BDDMA-based vinylester matrix (above) and styrene-based matrix (below).  
at left:Tomography micrograph, right : same image after thresholding showing porosities and cracks in white**

## CONCLUSION

The interface is a key component which governs the mechanical behavior of fiber-based composite materials. In this work, the nature of the interface was investigated *i/* at the molecular and single fiber scale, *i.e.* considering sizing and its interactions between the different components of vinylester-based resins as well as micromechanics involving microdroplet debonding; *ii/* at macroscale from analyses performed on unidirectional composite materials. The role of the solubility of the sizing into the reactive diluent, styrene or BDDMA, was evidenced. The conventional interfaces made in presence of styrene-monomer seem to be quite relevant at fiber scale and even at composite scale. The high solubility of sizing in styrene ensures a good wettability required to create an intimate contact with the fiber during the impregnation step. According to the volatility and health issues related to the styrene-monomer, this one was substituted by 1,4-butanediol dimethacrylate in vinylester matrix. Thus, the capability of BDDMA-based (styrene-free) matrix for E-glass fiber impregnation and interfacial adhesion in SMC composites was evaluated. Wettability analyses revealed large differences between the two matrices. Styrene-free matrix displays a lower ability than vinylester-polyester matrix to wet sized E-glass fibers having vinylester-compatible sizing. However, micromechanical analysis shows a better stress transfer from the matrix to the fiber by using the styrene-free matrix. As BDDMA is far less volatile than styrene, the difference of IFSS values obtained from the two types of vinylester matrices using the microdroplet debonding test is impacted. Nevertheless, by considering unidirectional composites, it was clearly evidenced that the compatibility between the glass fiber and BDDMA-based matrix needs to be improved. Short-beam flexural test allowing to quantify ILSS evidenced a significant difference between the two types of vinylester matrices.

All the analyses developed to compare two types of vinylester matrix used in SMC formulations showed the limits of styrene-free, *i.e.* BDDMA-based matrix, in terms of fiber wettability and resulting interfacial adhesion. These results show the needs for development of BDDMA-compatible sizing for glass fiber used in SMC composites in order to replace styrene in formulations. Further

works will be dedicated for designing sizings which will be more compatible with methacrylate-based diluents in order to generate an intimately built and efficient fiber/matrix interface.

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