

# MULTISCALE INTERPHASE INVESTIGATION OF SIZED GLASS FIBER / THERMOSET COMPOSITES

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## ABSTRACT

Materials are characterized under thermal and thermomechanical solicitation at multiscales. The reinforcement has been studied separately on the vinylester and epoxy matrix composites. The sizing evolves with time, owing to exudation of small plasticizer molecules or film former polymerization. In the current paper, a series of unidirectional composite plates are reinforced with different treated glass fibers. These model interphases were useful to access to a better understanding of the interphase formation. Microthermal analysis shows that the glass transition temperature decreases at decreasing distance from fiber surface. The matrix nature influences the interphase width.

## 1. INTRODUCTION

Thermosetting based composite have higher mechanical and thermomechanical characteristics at the initial state. For their aeronautic applications, composite structures have to keep these good functional characteristics under mechanical and environmental solicitations. There is a great diversity of physical and chemical effects with complex interactions; nevertheless the degradation of the interfacial zone is commonly retained to be the major cause of the damage in mechanical properties [1, 2]. Before analyze the effects of ageing, the intherphase must be considered at the initial stage These last thirty years and always current, the emphasis was especially put on the understanding, the control and the promotion of matrix / reinforcement interface, with sizing of different natures [3, 4]. But in-situ interphase study is restricted by means and scales of analysis. This project aims to improve knowledge of the physicochemical phenomena occurring in the interphase. In order to follow the influence of glass surface treatment, some model interphases composites are carried out. The objective of this study was to monitor macromolecular mobility at different scales thanks to various techniques giving either global or local response.

## 2. EXPERIMENTS

E-glass fibers with different treatments and resulting composites with model interphases have been used to examine the interphase in commercial sized fibres composites. E-glass fibers have been supplied by Saint-Gobain Vetrotex International. These fibers (300 Tex, 14  $\mu\text{m}$ ) have been treated with a commercial sizing known as « universal sizing », i.e. suitable for epoxy as well as vinylester matrices. This sizing contains also two types of coupling agents, a complex aminosilane and a methacrylsilane.

The thermosetting matrix are a DGEBA-based epoxy resin (Araldite® LY556 from Ciba-Geigy) with aliphatic polyamine (XB3486 from Huntsman) selected as hardener at 33 parts by weight of resin, and also a DGEBA-based vinylester (Derakane 411-350 from Ashland) with catalytic system (peroxide initiator (Butanox M50) and accelerator NL-51P and promoter C from Akzo Nobel). These resins have a long pot life

compatible with the filament winding process at ambient temperature used to obtain laminas.

Some material configurations using different treated fibers were investigated (Table 1). The plates were manufactured either by filament winding for high volume fraction of glass or moulding for low volume fraction. The composites were cured according to the supplier's recommendations in order to obtain maximal conversion.

Composite		<i>Types of fibers</i>	<i>Weight fraction of glass (wt%)</i>	<i>Volume fraction of glass (vol%)</i>	<i>Process</i>
Epoxy-aliphatic	EP-CS50	<i>Commercial Sizing</i>	70(±2)	50(±1)	<i>Filament winding</i>
	EP-CS20	<i>Commercial Sizing</i>	28(±3)	20(±3)	<i>Moulding</i>
	EP-TD15	<i>Thermally Degraded</i>	21(±2)	15(±2)	<i>Moulding</i>
Vinylester	VE-CS54	<i>Commercial Sizing</i>	72(±1)	54(±1)	<i>Filament winding</i>
	VE-CS20	<i>Commercial Sizing</i>	27(±4)	20(±3)	<i>Moulding</i>
	VE-TD15	<i>Thermally Degraded</i>	20(±3)	15(±3)	<i>Moulding</i>

Table 1: Composites characteristics and their corresponding abbreviations

Different techniques (MDSC, DMA,  $\mu$ TA) allow us to characterize the molecular mobility at different scale. The dynamic mechanical response is a true signature of the material state. Other characterizations are carried out at the same time to be able to get more information, particularly at microscopic scale with thermal microanalysis. A fine study of the model interphase is undertaken in order to join together precise informations on the extent and structure of this interfacial zone.

Modulated differential scanning calorimetry enables to separate the reversing thermodynamic phenomena from the non-reversing kinetic phenomena. Moreover, a quantitative measurement of heat capacity jump ( $\Delta C_p$ ) during glass transition can be performed. Experiments were performed in aluminium standard pans on a MDSC Q100 from TA Instruments. The glass transition temperatures  $T_g$  were measured at a heating rate of  $2^\circ\text{C}\cdot\text{min}^{-1}$ , superimposed to a modulation amplitude of  $\pm 1^\circ\text{C}$  per period of 60 seconds.

Dynamic mechanical analysis (DMA) was used to measure the mechanical properties (modulus and damping ( $\tan \delta$ )) of materials as a function of temperature at single frequency. Tests were conducted on a DMA 2980 from TA Instruments in single cantilever mode. Temperature of main relaxation process  $T_\alpha$  was taken at the maximum of damping spectrum recorded at  $2^\circ\text{C}\cdot\text{min}^{-1}$  between ambient and  $160^\circ\text{C}$ . In order to characterize preferentially fiber /matrix interface, composites were solicited perpendicular to fiber direction at single frequency of 1 Hz and displacement amplitude of  $7 \mu\text{m}$ . This last value was chosen to be in linear viscoelastic range of each sample. The characterization of sizing viscoelastic behaviour is described in [5] and [6]. Miller [6] developed a technique to characterize sizing by soliciting sized glass fibers. The glass strands are placed between rigid supports in dual cantilever deformation mode. The deformation is applied on bundles of sized fibers sandwiched between two steel plates (thickness  $\sim 100 \mu\text{m}$ ). Thus, this particular assembly allows investigating sized fibers at a cooling rate of  $2^\circ\text{C}\cdot\text{min}^{-1}$  from  $80^\circ\text{C}$  down to  $-50^\circ\text{C}$ , a single frequency of 1 Hz and displacement amplitude of  $140 \mu\text{m}$ .

Micro-thermal analysis combines the visualisation and positioning methods of atomic force microscopy (AFM) with the technology of thermal analysis with a thermoresistive probe [7]. The localized thermal analysis allows the gradient of properties existing from fiber towards bulk matrix to be characterized. A  $\mu$ TA 2990 from TA Instruments micro-thermal analyser was used. The experiment consists in following the deflection in sensor position associated to the glass transition in the vicinity of the fiber-matrix interface, during a heating ramp from ambient temperature to 250°C at 10°C.s<sup>-1</sup>. A contact force of 100 nN was used for our thermosets materials. A change in slope (d $\Delta z$ /dT) corresponds to a softening temperature  $T_s$  associated to the glass transition of the polymer. We reported the temperatures vs distances from glass fiber surface. Plates were cross-sectioned and polished to establish detailed cartography.

### 3. EXPERIMENTAL RESULTS

#### 3.1 Sized E-glass fibers

The glass transition temperatures of sized glass fibers were determined by DMA to follow Miller's method [6]. A relaxation phenomenon is observed with a peak on damping (tan  $\delta$ ) for commercial fibers spectra, unlike thermally degraded fibers (see Figure 1). The sensitivity of the technique is validated on detecting the relaxing fraction of sizing. Sizing fraction is 0.50 ( $\pm 0.05$ ) %wt determined by loss on ignition during 1h30 at 110°C following calcination at 625°C during 20 min. We have followed the damping response of varying numbers of glass strands between the clamps (Figure 1). The evolution of damping and area linked to an amount of dissipated energy is proportional to a sizing weight until 50 glass strands. The last data is no longer proportional to the amount of sizing because the glass disturbs the sollicitation; the assembly becomes too stiff.

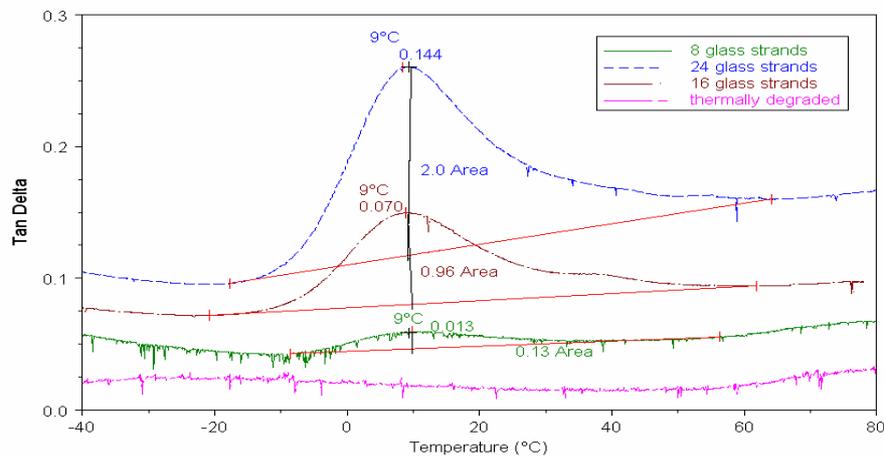


Figure 1: Evolution of damping for commercial sized fibers with increasing number of glass strands (single cantilever, 2°C.min<sup>-1</sup>, 1Hz, 140 $\mu$ m). The curves are vertically shifted for readability criterion.

It should be noted that the glass transition temperature of sized glass fibers is shifted towards the high temperatures with the time. The  $T_g$  of these recent spinning commercial sized fibers is significantly lower (Figure 2). Thus the sizing at fibers surface evolves during time. The damping value or area associated to dissipated energy is lower 16 months later for the same number of glass strands. Relaxing entities

quantity decreases. It can be explained by the decrease of relaxing entities quantity, resulting from the exudation of small molecules from components acting as plasticizers. It can also be linked to the polymerization of epoxy film former.

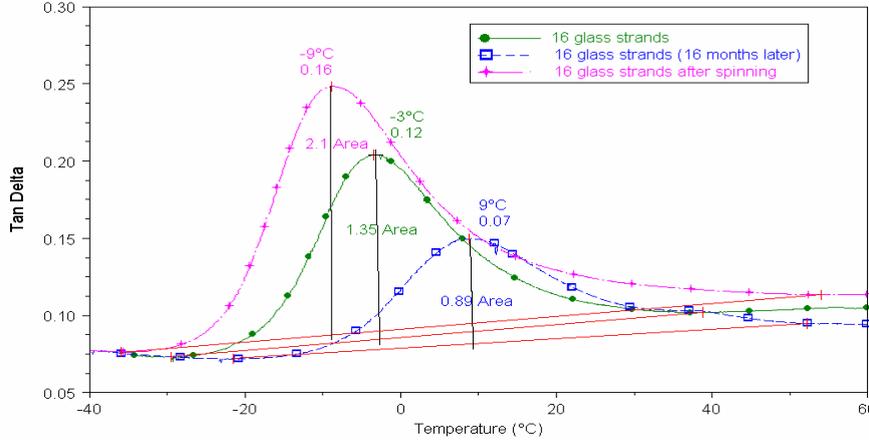


Figure 2: Evolution of damping of commercial sized glass fibers with ageing (single cantilever mode,  $2^{\circ}\text{C}\cdot\text{min}^{-1}$ , 1 Hz,  $140\ \mu\text{m}$ )

### 3.2 Unidirectional composites

We focused on a better understanding of the polymer network formed at the sized glass fibers/thermosets matrix interphase. Thermal and dynamic mechanical analysis didn't reveal great variation in glass transition temperature, but several changes occur in relaxation process amplitude. Recent researches at interphase scale have shown that this region can be significantly influenced by the presence of coupling agent or other sizing components at the surface of reinforcement, which can disturb the curing process [8, 9].

#### 3.2.1. Interphase thickness estimation by thermal analysis

Modulated differential scanning calorimetry, more precise than classic DSC, gives access to temperature and jump in thermal capacity ( $\Delta C_p$ ) during glass transition. This last data could be used to evaluate the interphase thickness  $e$ , thanks to an empiric formula published by Lipatov [10], which leads in the case of unidirectional composite to the following expression (Eq.1):

$$e = r_{\text{fiber}} \left\{ \left[ \left( 1 - \frac{\Delta C_p^c}{\Delta C_p^m} \right) \left( \frac{V_f}{1 - V_f} \right) + 1 \right]^{1/2} - 1 \right\} \quad (1)$$

where  $r_{\text{fiber}}$  and  $V_f$  are respectively fibers average radius and volume fraction.  $\Delta C_p^m$  and  $\Delta C_p^c$  are matrix and composite jump of  $C_p$  respectively, measured on MDSC thermograms. Lipatov's works indicate that  $\Delta C_p$  reduction is linked to the interaction between a fraction of matrix macromolecules and the surface of the reinforcement. These macromolecules are thus excluded from cooperative process governing the glass transition phenomenon. Indeed,  $C_p$  jump during transition is a decreasing function of cross-link density. Thus, an increasing density associated to a decreasing number of possible network configurations, leads to a lower  $\Delta C_p$ . We also observed a decrease in the  $\Delta C_p$  with increasing fiber fraction, but similar  $T_g$  for the composites, except for

thermally degraded fibers epoxy composite (EP-TD15) which shows a slightly higher  $T_g$ . The  $\Delta C_p^c$  for slightly reinforced composites are close to the  $\Delta C_p^m$  for matrix with standard deviation of measurements. The effective thickness of interphase was estimated from the consideration of differential heat capacity jump between fiber-reinforced and unfilled resins in the glass transition [10]. The interphase thickness is estimated at 1.7  $\mu\text{m}$  for composite EP-CS50 and 2.1 $\mu\text{m}$  for composite VE-CS54, according to Eq.1. Table 2 lists the thermal data and estimated interphase thickness. Kim & al. [11] used the thermal capacity jump measurements, nanoindentation and nanoscratch tests for investigation of the interphase in glass fiber reinforced vinylester matrix composites with different silane treatments. The interphase thickness values are 1.5  $\mu\text{m}$  for methacrylsilane and 1.6  $\mu\text{m}$  for epoxysilane. The results obtained on the heat capacity measurements agreed with those obtained from nanoscratch tests in qualitative terms, but also suggested that the former method was more sensitive to a small change in chemical structure within the interphase than the nanoscratch test. Similarly, Lagache [12] applied this equation to different fractions of reinforcement in unidirectional composites with matrix epoxy-anhydride reinforced with aminosilane ( $\gamma$ -APS) sized glass fibres (300 Tex, 14  $\mu\text{m}$ ). The thickness of the interfacial zone is about 2.2  $\mu\text{m}$  for fibres volume fraction of 50%, 1.3  $\mu\text{m}$  for 30%vol. and 0.6  $\mu\text{m}$  for 15%vol. According to these thicknesses, the fractions of modified matrix are 3, 12 and 37%. The proportions of modified matrix according to our thickness and homogeneous surface assumption, are reported in the last column of table 2. These values suggest an increasing proportion of matrix disturbed by the reinforcement. The matrix proportion for strongly reinforced composite is about 36% for vinylester system whereas for epoxy-aliphatic, about 27%.

		$T_g^{m \text{ or } c}$ ( $^{\circ}\text{C}$ )	$\Delta C_p^{m \text{ or } c}$ ( $\text{J}/(\text{g}\cdot^{\circ}\text{C})$ )	$e$ ( $\mu\text{m}$ )	Modified matrix amount
Epoxy aliphatic	resin EP	98( $\pm$ 4)	0.20( $\pm$ 0.05)		
	EP-CS50	101( $\pm$ 1)	0.09( $\pm$ 0.05)	1.7( $\pm$ 0.7)	27%
	EP-CS20	102( $\pm$ 2)	0.15( $\pm$ 0.05)	0.2( $\pm$ 0.1)	1.3%
	EP-TD15	105( $\pm$ 2)	0.18( $\pm$ 0.05)	0.06( $\pm$ 0.02)	0.3%
VinylEster	resin VE	112( $\pm$ 2)	0.21( $\pm$ 0.04)		
	VE-CS54	114( $\pm$ 1)	0.09( $\pm$ 0.05)	2.1( $\pm$ 0.9)	36%
	VE-CS20	112( $\pm$ 2)	0.15( $\pm$ 0.05)	0.3( $\pm$ 0.1)	1.4%
	VE-TD15	111( $\pm$ 2)	0.20( $\pm$ 0.05)	0.03( $\pm$ 0.01)	0.1%

Table 2: MDSC results and calculation from Eq.1 ( $2^{\circ}\text{C}\cdot\text{min}^{-1}$ )

### 3.2.2. Interphase characterization by thermomechanical analysis

Using dynamic mechanical analysis (DMA), we have been able to confirm the thermal analyses (MDSC). Table 3 gathers the dynamic mechanical results. The commercial sizing epoxy composites (EP-CS50 and 20) show main relaxation temperatures  $T_{\alpha}$  close to the resin one, whereas the EP-TD15 composite shows a higher  $T_{\alpha}$ . This effect may be attributed to surface treatments which induce a lower cross-link density network

and/or plasticize, which compensated the reduction of mobility due to the presence of reinforcement.

For vinyl ester system,  $T\alpha$  is similar for all. Figure 3 (a and b) shows damping spectra ( $\tan \delta$ ) for each system with a Gaussian profile, characteristic of a perfectly crosslinked network.

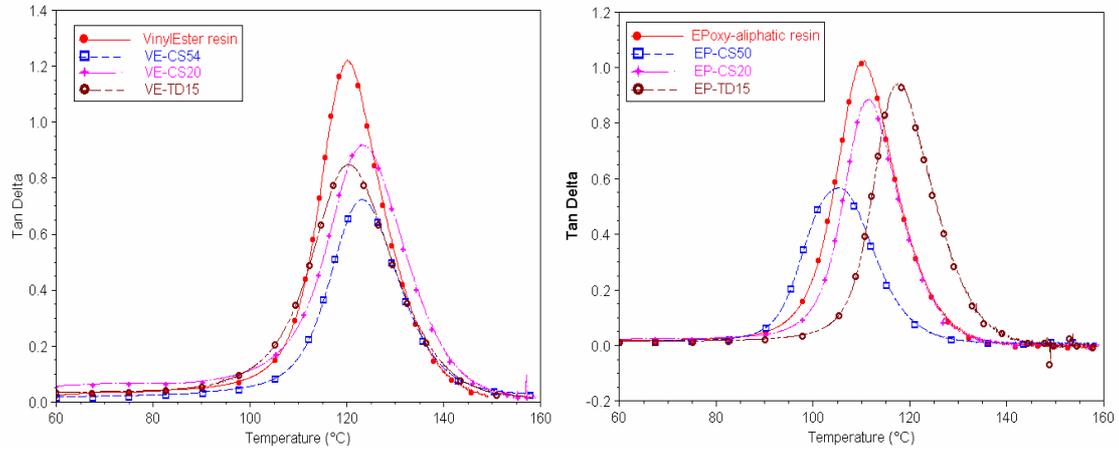


Figure 3: Composites and resin damping spectra for Epoxy-aliphatic and VinylEster system (single cantilever mode,  $2^{\circ}\text{C}\cdot\text{min}^{-1}$ , 1 Hz, 7  $\mu\text{m}$ )

We note a decrease of damping which is not directly proportional to the volume fraction of matrix. The damping of the composite cannot be predicted from the simple law of mixtures according to  $\tan \delta_c = (1-V_f) \tan \delta_m$ ; that underestimates the value because of the interphase existence.

		$T\alpha$ ( $^{\circ}\text{C}$ )	$\tan \delta_{c \text{ or } m}$
Epoxy- aliphatic	resin EP	108( $\pm 3$ )	1.02( $\pm 0.05$ )
	EP-CS50	105( $\pm 1$ )	0.57( $\pm 0.01$ )
	EP-CS20	111( $\pm 3$ )	0.90( $\pm 0.05$ )
	EP-TD15	115( $\pm 2$ )	0.95( $\pm 0.05$ )
vinylester	resin VE	120( $\pm 2$ )	1.18( $\pm 0.02$ )
	VE-CS54	121( $\pm 2$ )	0.76( $\pm 0.03$ )
	VE-CS20	123( $\pm 1$ )	0.87( $\pm 0.07$ )
	VE-TD15	120( $\pm 1$ )	0.86( $\pm 0.02$ )

Table 3: DMA data ( $2^{\circ}\text{C}\cdot\text{min}^{-1}$ , average values obtained from 2 to 5 samples)

### 3.2.3. Microthermal analysis in the interphase

For composites, imaging mode is used to obtain a surface cartography of polished specimens, allowing the localised thermal analysis (LTA) at increasing distances from monofilaments. The topography and conductivity images are obtained simultaneously by scanning surface at constant force. The temperature is fixed at  $50^{\circ}\text{C}$  in order to increase the contrast of thermal conductivity between polymer matrix and glass reinforcement. On 2-D mappings, strategic points at increasing distances from monofilaments were selected (see Figure 5). The typical response of sensor is done in Figure 6.

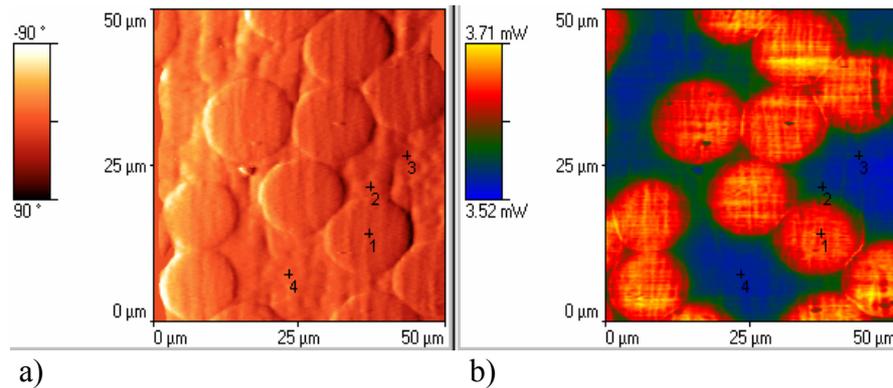


Figure 5:  $\mu$ TA on strongly reinforced composite (VE-CS54): (a) isoform topographic scan and (b) isothermal (50°C) apparent thermal conductivity scan

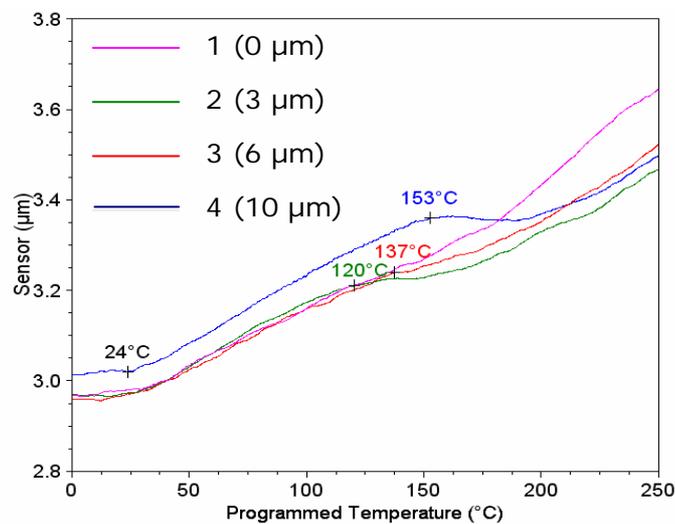


Figure 6: Typical LTA measurement of the local softening point for vinyl ester matrix of composite VE-CS54 ( $10^{\circ}\text{C}\cdot\text{s}^{-1}$ )

We reported softening temperature for each LTA measurements vs distance from monofilament in order to follow the gradient of softening temperature in composite. Figures 7 and 8 (a and b) shows LTA results in statistical distribution according to the distance to monofilaments for each composites. Different  $T_s$  measurements on resin have been performed and superimposed for comparison. The interphase region influenced by sizing is characterized by a softening temperature lower than the one of surrounding matrix. The dispersion of results is explained by heterogeneities of cross-link density and by heterogeneous sizing distribution on fibres. Many studies [5, 13] report that sizing distribution is not uniform in three dimensions. The agglomerates described in literature [14] as “silane islands” are clearly visible on the fibres surface by AFM.

In the case of vinyl ester composite, the interphase is present for each treatment of fibers and extends over  $15\ \mu\text{m}$  (see Figure 7). Kim [11] saw the presence of interphase in the case of a non compatible organosilane with matrix, i.e. epoxysilane fiber reinforced vinyl ester matrix composites. Dirand [15] showed that the crosslinking network was disturbed at the vicinity of glass substrate, whatever the surface treatment (sized or not).

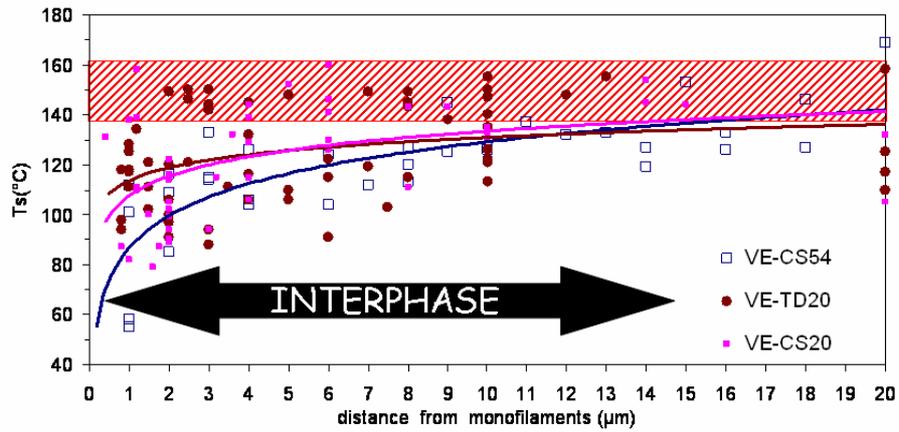
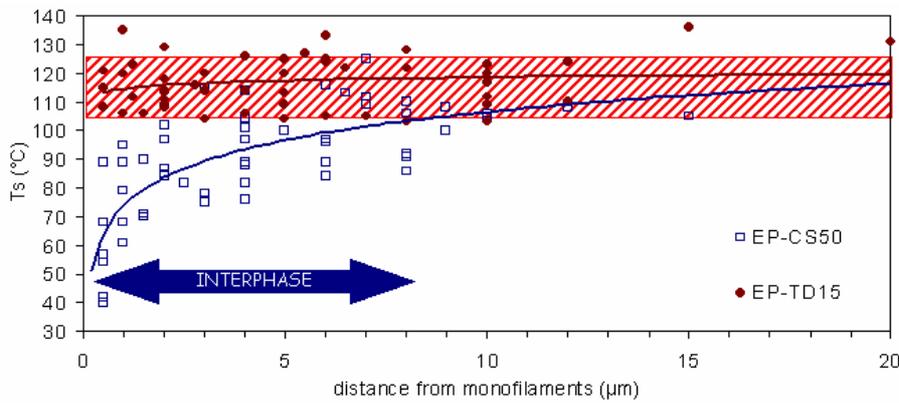
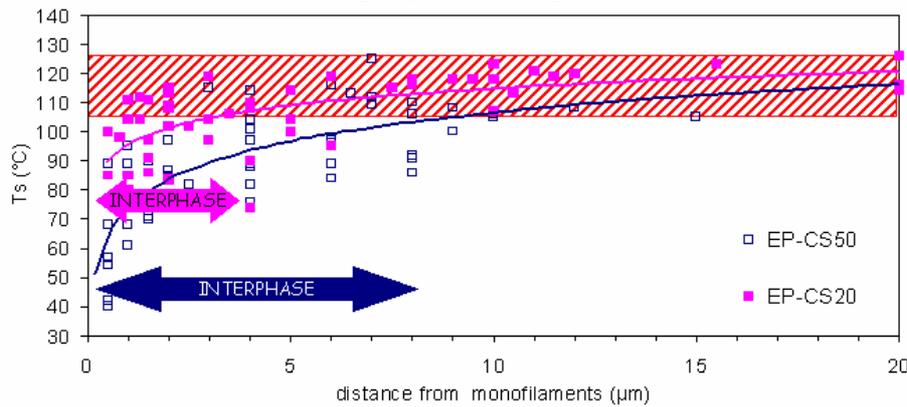


Figure 7:  $T_s$  evolution vs distance from monofilament for vinylester composite with bulk resin (  ) as reference



a) highlight of interphase



b) influence of fibers fraction

Figure 8:  $T_s$  evolution vs distance from monofilament for epoxy-aliphatic composite with bulk resin (  ) as reference

Cross & al. [8] used fiber-optic evanescent wave FTIR spectroscopy combined with phase imaging AFM, which allows to examine interphase in-situ like  $\mu$ TA. The spectroscopic results showed incomplete curing in the vicinity of the fibre for an epoxy/ acid anhydride system, exhibiting a 2.5 micrometer thick interphase region, comparable to our values. Consequently, the presence of interphase is attributed to an incomplete

curing next to fibre. This effect is marked on strongly reinforced composite (EP-CS50) and more restricted for slightly reinforced composite (EP-CS20) (Figure 8b). The interphase of EP-CS50 composite extends up to 8  $\mu\text{m}$ , and for EP-CS20 composite not more than 4  $\mu\text{m}$ . Volume fraction of sized fibres influences the interphase organization. Thus, the reduction of interphase width could be induced by steric effects which accentuates the under-curing. "Cleaned" fibers reinforced composite results confirm the absence of interphase when sizing is removed from fibers in the epoxy system. The evidence of an under-curing due to surface treatment is reinforced. For epoxy-aliphatic composite strongly reinforced with commercial glass fibers, the softening temperature decreases about 60°C from the matrix at decreasing distance from the fiber surface. For vinylester composite, the  $T_s$  fall is about 80°C. The influence of other secondary agents should be also taken into account. Gorowara & al. [13] brought back that some auxiliary components would remain in higher concentrations in the interphase. The concentration of nonreactive species in the interphase would reduce the network crosslink density.

#### 4. CONCLUSION

Clearly, the formation of interphase is associated to the chemistry of matrix. The effects of macromolecular mobility in the interphase are different from matrix due to crosslinking process. On the one hand for epoxy, it consists in a polyaddition reaction of amine hardener with resin. According to hardener affinity with surface of glass fiber, there is a stoichiometric gradient. On the other hand for vinylester, the crosslinking reaction is radical copolymerization. Styrene, in the monomeric form, acts as resin diluent and as monomer reacting with prepolymer. Styrene in solvent function diffuses and evaporates. These are many motive mechanisms for stoichiometry imbalance.

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