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Relationships between the glass fibre sizing composition and the surface quality of sheet moulding compounds (SMC) body panels

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Abstract

The characteristics of thermosetting composite materials such as SMC are affected by the presence of reinforcements as a result of surface–matrix interactions. Surface treatments or sizings can significantly affect such interactions; hence the sizing selection may significantly affect SMC characteristics. The wetting properties of the unsaturated polyester matrix on glass fibres with different sizings have been studied by contact angle determination. In addition, the permeability of the glass fibres as well as their stiffness, the sizing solubility and swelling were also studied to understand the impregnation level of the glass fibres by the unsaturated polyester matrix before the curing reaction as a function of the sizing chemistry. The parameters that have been varied to determine the wetting and the adhesion properties provided by surface energies are the followings: (i) the sizing amount; (ii) the antistatic agent nature; (iii) the deposit method of this antistatic agent, and (iv) the film former nature. From these results in relation with the surface quality of corresponding moulded SMC panels, some of these glass fibres were selected. By using a statistical approach (principal components analysis (PCA)), it has been possible to conclude about the influence of the glass fibres characteristics on the surface quality. Correlations have also been established between the glass fibre characteristics, the material flow and the surface quality of the SMC panels.

Keywords: Glass fibre; Sizing; Permeability; Solubility; Stiffness; Surface quality; SMC

1. Introduction

Since the advent of silane coupling agents as a pre-treatment of glass fibres to improve the durability of glass fibres, a lot of researches have been conducted to give more informations on the chemistry of the silanes and on the interactions between the glass fibre surface and the matrix [1–6]. Nevertheless silanes represent only a small fraction of the sizing system and the extrapolations made with the silane behaviour on glass fibre/matrix adhesion neglect the potential effects of the presence of the other components (lubricants, film formers and

antistatic agents). To optimize SMC performances, not only the resin and the fibre should be taken into account but also the sizing nature that leads to the formation of an interphase, which affects the global composite behaviour. This behaviour can be influenced by the processing conditions such as the resin viscosity, the time to gelation, the kinetics of cure... [6–11]. The more uniform and continuous the impregnation process, the better the surface quality of SMC. A poor impregnation will give a poor adhesion and will induce the formation of voids. This will generate defects on the SMC panel surface. The surface quality is defined by the waviness of the panel surface (called Diffracto Index) and by the number of defects as pinholes, bubbles and craters. This surface quality can be influenced by the SMC

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components (fibre and organic matrix), by the moulding parameters but also by the glass fibre/organic matrix interactions. The study of the influence of these parameters needs to be developed. We have seen in a previous work [12] that the use of different sizing systems for glass fibres may modify the glass fibre characteristics and thus the wetting properties and the surface quality of the corresponding moulded panels.

Therefore, in the present work, the influence of the sizing composition of the glass fibre on the wetting properties of the fibres and the fibre/SMC paste adhesion before the curing of the SMC paste has been studied. In order to vary the sizing composition of the glass fibres, different antistatic agents deposited through various methods and different film formers have been used. Moreover the influence of the sizing contents have been studied. From this preliminary analysis, some glass fibres were selected in relation with the surface quality of the corresponding moulded SMC panels. After that, other characteristics have been introduced such as the permeability of a glass fibre mat, the fibre bundle stiffness, the solubility and swelling ability of the sizing systems to carry out a statistical analysis based on principal components analysis (PCA) and to establish correlations between the different glass fibre characteristics and the surface quality of the moulded SMC panels but also the SMC paste flow during moulding.

2. Materials and techniques

2.1. Materials

Different sizing systems were provided by Saint Gobain Vetrotex International (Chambéry, France) with confidential formulations. Nevertheless the antistatic agents and the film formers chemical nature will be detailed as shown in Tables 1–3. It can be noticed that the sizing amount applied onto the fibre surface (Table 1) but also the deposit method of the antistatic agents have been considered as variable parameters (Table 2). The first deposit method is a classical one where the antistatic agents are introduced within the sizing solution before the fibre to be sized. The second deposit method consist in applying the antistatic agents in a second separate step after the other components of the sizing systems have been deposited on the fibre.

Table 1
Sizing amount applied onto the fibre surface (%)

Fibre	Sizing amount (%)
1	1.38
2	1.59
3	1.79

The SMC polyester paste used for this study was provided with a confidential composition to investigate the effects of glass sizings on the fibre wetting properties, on the fibre/matrix adhesion and on the surface quality.

2.2. Techniques

2.2.1. Contact angle measurements

Contact angle measurements of the sized glass fibres were performed using a KSV LPR902 of KSV Instruments. The fibres were cut at 9 mm and samples of 7 g and were packed into a glass cylinder. Contact angle measurements of the matrix SMC were performed using a DIGIDROP of GBX Instruments, which allows an automatic formation of a liquid droplet on the SMC matrix. The wetting liquids used for contact angle measurements during the test were *n*-hexane, water, toluene and ethylene glycol.

2.2.2. Permeability measurements

During the impregnation of the glass fibres by the matrix, two phenomena may occur which are the wet-through and the wet-out. The wet-through phenomenon corresponds to the passage of the resin into the fibres network. The wet-out phenomenon corresponds to the progressive wetting of each filament of the glass fibres and to the partial solubilization of the fibre sizing during compression moulding. The wet-through phenomenon is mainly governed by the initial permeability of the fibre mat, which depends on the fibre physical characteristics such as the fibre stiffness. To evaluate this permeability of the fibre mat, an experimental unit has been adapted on a standard air permeabilimeter. A pump sucks up the air at an adjustable pressure through the unit furnished with a defined area circular opening. A sample with a given mass per unit area is put on the unit. The measured air flux (in $l\ s^{-1}\ m^{-2}$) corresponds to the permeability of the fibre mat.

2.2.3. Solubility

The soluble fractions of the glass fibre coating were measured according to ISO 11667 [13]. A minimum of three samples was used in each determination. Styrene was selected as an extraction solvent to serve as a solubility model for the matrix of interest. The extraction conditions were optimized in a previous work [12] (6 h, room temperature). The sizing solubility percentage is given by the following equation:

$$S(\%) = \frac{m_0 - m_1}{m_0 - m_2} \times 100, \quad (1)$$

with m_0 and m_1 , weights of fibres before and after extraction, and m_2 , weight of fibres after calcination at $625 \pm 20\ ^\circ\text{C}$ during $30 \pm 5\ \text{min}$.

Table 2
Antistatic agents used onto the fibre surface and the corresponding deposit method

Fibre	Type of antistatic agent	Deposit method
4	None	Classical sizing
5	Quaternary ammonium chloride	Oversizing
6	Quaternary ammonium sulphate 1	Oversizing
7	Quaternary ammonium sulphate 1 + fluorinated component	Oversizing
8	Quaternary ammonium sulphate 2	Oversizing
9	Quaternary ammonium chloride	Classical sizing
10	Quaternary ammonium sulphate 1	Classical sizing

Table 3
Film formers and antistatic agents used onto the fibre surface

Fibre	Type of film former	Type of antistatic agent
11	Highly unsaturated	No antistatic agent
12	Highly unsaturated	Quaternary ammonium sulphate 1 + fluorinated component
13	Bisphenolic, aromatic	No antistatic agent
14	Bisphenolic, aromatic	Quaternary ammonium sulphate 1 + fluorinated component
15	No bisphenolic, aromatic	No antistatic agent
16	No bisphenolic, aromatic	Quaternary ammonium sulphate 1 + fluorinated component

2.2.4. Fibre bundles stiffness

Stiffness measurements have been carried out through an industrial test used by Saint-Gobain Vetrotex International called the “nail test”. For this test, a fibre bundle with a given length (400 mm) is put on a nail (Fig. 1). The resulting distance x (mm) between the two extremities of the bundle is related to the stiffness of the fibre bundle. Indeed it seems obvious that the shorter this distance, the stiffer the fibre bundle because of the influence of the gravity which produces the bending of the fibre bundle.

2.2.5. Dielectric measurements

A dielectrometer (DEA 2970 TA Instruments) was used for dielectric measurements. The variations of the ionic conductivity, the loss factor and the permittivity were measured using a 30 Hz input signal versus temperature. The dielectric sensor was calibrated before the applying of the sizing film. For the preparation of the sizing film sample, a droplet of the sizing solution has been put on the sensor face. The sensor was heated to 130 °C for 4 h to form a thick film and slowly cooled to room temperature before testing. Two successive steps were provided. First, a data acquisition was made during 10 min at 25 °C, using a 30 Hz signal input, to stabilize the dielectric

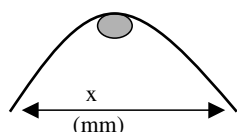


Fig. 1. Description of the “nail test”.

response of the sizing film prior to styrene contact. The second step is an isothermal treatment at 25 °C during 100 min after styrene contact using the same frequency.

2.2.6. Moulding parameters

Saint-Gobain Vetrotex Italia provided the SMC charge patterns used in the present investigation. The length of the glass fibres was 25 mm and the weight ratio about 28%. A compression moulding system (Rhonalp System, 400 tons) provided by Compositec (Le Bourget du Lac, France) was used. The dimension of the mould was 500 × 500 mm². The initial SMC charge pattern was 30% to make a final thickness of 2 mm. The mould was equipped with a mirror polish punch. The matrix surface temperature and the punch surface temperature were respectively 150 ± 1 and 145 ± 1 °C. The closure speed was 300 mm/s, the work speed 7 mm/s. The pressure has been kept at 70 bars with a cycle time of 100 s. For each test six panels were used to obtain a relevant averaged evaluation of the surface quality. Once the SMC panels moulded, the surface aspect was determined. For this evaluation, a Diffracto Sight AS-2 apparatus was used. It represents a tool to detect the waviness. The measure is based on an optical method: a white light beam is projected on the panel, reflected on a mirror opposite to the light source and returned back to the panel where it is recorded by a camera. This image is compared to a reference panel and a Diffracto index is given. A good surface aspect corresponds to a low Diffracto index [14]. The other defects like pinholes, craters and bubbles were evaluated by visual human counting.

3. Determination of different characteristics of the glass fibres

3.1. Surface free energy of sized glass fibres

Contact angle measurements of the sized glass fibres were provided as described in a previous work [12] using Washburn's equation [15]:

$$t = \left[\frac{\eta}{C \cdot \gamma_L \cdot \cos \theta} \right] V^2, \quad (2)$$

where t is the time after contact, η the liquid viscosity, C a material constant independent of the used liquid, γ_L the surface free energy of the liquid, θ the contact angle and V the liquid volume absorbed on the solid.

The geometric approach proposed by Owens et al. [15,16] has been used to investigate the surface free energy of the sized glass fibres:

$$\gamma_L(1 + \cos \theta) = 2 \cdot \sqrt{\gamma_S^D \cdot \gamma_L^D} + 2 \cdot \sqrt{\gamma_S^P \cdot \gamma_L^P}, \quad (3)$$

where the subscripts L and S are related, respectively, to the liquid and the solid states, D and P the dispersive and polar characters.

The impregnation of the fibres by the SMC paste and thus the fibre/matrix adhesion could be evaluated according to the following conditions:

- (1) an optimal wetting may be obtained if the γ_S value of the fibre is superior to the γ_S value of the SMC paste,
- (2) an optimal adhesion is obtained if the dispersive and polar components of the fibre are close to those of the SMC paste.

Based on these conditions, the influence of the sizing amount applied onto the fibre surface, of the nature and of the deposit method of the antistatic agent and of the film former nature has been studied. Then the variations of the surface properties of the glass fibres after extraction in styrene have been determined.

3.1.1. Surface properties of sized fibres

3.1.1.1. Influence of the sizing amount applied onto the fibre surface. To increase the sizing amount applied onto the fibre surface, the film former content has been increased, the other components contents remaining constant. The corresponding film former is based on polyvinylacetate (PVAc). The influence of the sizing amount on the surface energy of the glass fibres has been studied for 3 sizing amounts from 1.38 to 1.79 wt % (Table 1) as shown on Fig. 2.

An optimized wetting of the fibre by the SMC paste seems to be obtained for the lowest sizing amount (1.38 wt%) as the adhesion seems to be better for a high sizing rates.

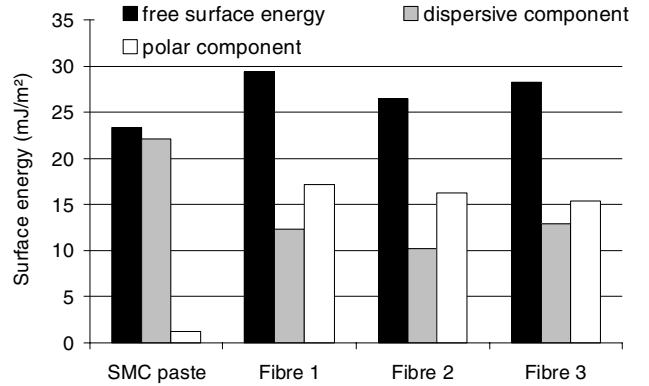


Fig. 2. Influence of the sizing amount applied onto the fibre surface on the surface energy of the glass fibres.

Moreover, the increase in the sizing amount seems to decrease the polar component of the surface energy of the glass fibres as the dispersive component remains constant. This result is in agreement with the surface properties of PVAc film former ($\gamma_S = 42.85 \text{ mJ/m}^2$, $\gamma_S^D = 27.40 \text{ mJ/m}^2$, $\gamma_S^P = 15.40 \text{ mJ/m}^2$) [17].

3.1.1.2. Influence of the nature and of the deposit method of the antistatic agent.

The different antistatic agents used are listed in Table 2. The choice of the antistatic agents is based on a previous study [12] where a quaternary ammonium chloride (fibres 5 and 9) and a quaternary ammonium sulphate (fibres 6 and 10) were used as antistatic agents. The fibre sizing has also been combined to a fluorinated component (fibre 7) because of its hydrophobic properties. The two previously described deposit methods of the antistatic agents were compared, on one side for quaternary ammonium sulphate (fibres 6 and 10) and for quaternary ammonium chlorine (fibres 5 and 9).

Results are presented in Figs. 3 and 4. Data show that the surface free energy increases when an antistatic agent is applied on the sized fibre surface.

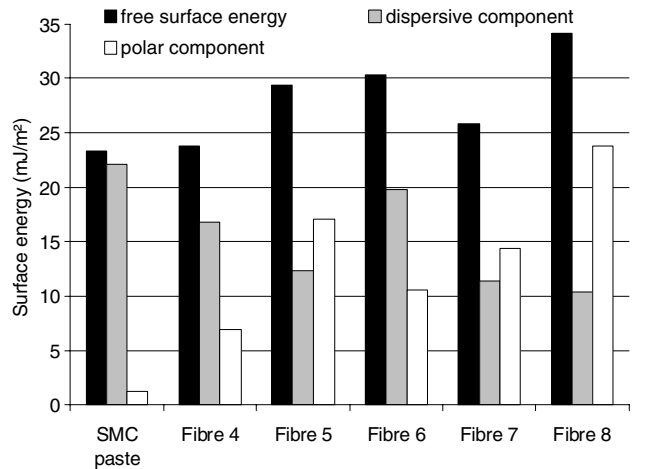


Fig. 3. Influence of the antistatic agent nature on the surface energy of the glass fibres.

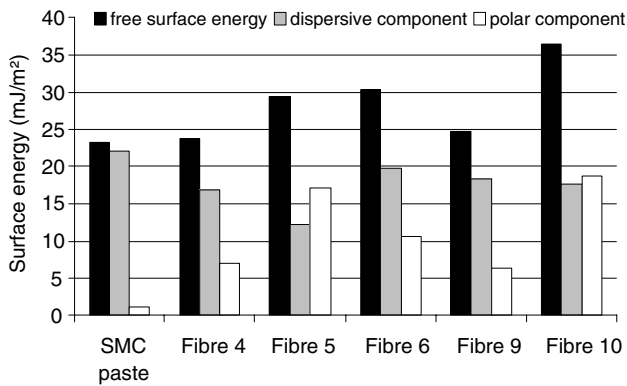


Fig. 4. Influence of the deposit method of the antistatic agent on the surface energy of the glass fibres.

The use of a quaternary ammonium chlorine (fibre 5) as an antistatic agent seems to provide a high free surface energy and a polar character.

The use of an antistatic agent based on a quaternary ammonium sulphate (fibres 6 and 8) seems to provide different surface properties according to their chemical nature.

When a fluorinated component is combined to the quaternary ammonium sulphate (fibre 7), a decrease in the free surface energy surface and an increase in the polar character of the fibre were obtained. As the fluorinated component is a hydrophobic component, we estimate that the addition of this component provides a dispersive character. Therefore the polar character of the fibre 7 seems to be linked to a potential reaction between the sizing components and the antistatic agents which modify the fibre surface properties.

As concerns the influence of the deposit method of the antistatic agent (Fig. 4) it can be observed that the addition of a chlorine agent (fibres 5 and 9) in two steps confers to the fibre a high free surface energy and a polar character due to the partial diffusion of this antistatic agent throughout the sizing layer. On the contrary, the addition of this chloride antistatic agent in one step provides to the fibre a strong dispersive character. Because of the dispersive character of the polyvinylacetate used as film former [17], it can be supposed that the antistatic agent diffuses more easily through the sizing in the case of a one step process and gives therefore the possibility to the polyvinylacetate to be at the fibre surface. In the case of the sulphate antistatic agent (fibres 6 and 10), opposite results have been obtained. This behaviour could be due to a different and more complex diffusion phenomenon of the antistatic agent into the sizing network. In fact, when the sulphate agent is deposited in one step (fibre 10) a higher polar character is obtained than when it is applied in two steps (fibre 6) even though the polyvinylacetate and the sulphate agent have both dispersive character.

Nevertheless, from the comparison between the surface properties of the different fibres and those of the SMC paste, it can be observed better wetting properties with the fibres 5, 6 and 10 and an optimal fibre/SMC paste adhesion for the fibres 9 and 6. Moreover it can be noticed that the fibre/SMC paste adhesion seems accurate when no antistatic agent is present in the sizing system (fibre 4), it is necessary to introduce an antistatic agent to confer antistatic properties to the fibres for a good fibre cutting.

3.1.1.3. Influence of the polyester nature. Fig. 5 shows that the film former nature and especially the type of polyester used has a major influence on the surface properties of the glass fibres. For this study, three kinds of polyester were used as film formers: (i) a highly unsaturated dialkylphthalate resin with a low polarity ($\gamma^P/\gamma < 0.2$) [18], (ii) a bisphenolic aromatic polyester commonly used for short strand mats and with a high polarity and (iii) an aromatic polyester with no bisphenolic functions and a high polarity.

Results show that the fibre 11 presents a high dispersive character due to the low polarity of the dialkylphthalate used as film former linked to the high dispersive solubility of this type of ester [19].

In the case of the fibre 12, the dispersive character displayed by the fibre 11 and due to the presence of the dialkylphthalate polyester is compensated by the polar character of the antistatic agent. This result seems to indicate that the diffusion of this agent through the sizing is low.

As concerns the fibre 13, the aromatic bisphenolic polyester addition provides to the surface fibre a polar character due to the partial solubility of this polyester in dispersive solvents as ketones and aromatics [19].

The high polar character of the fibre 15 surface can be explained by the partial solubility of the aromatic polyester in solvents as ketones, esters or aromatics which

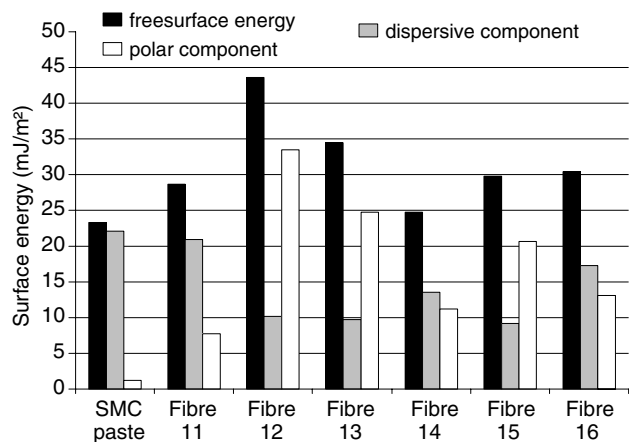


Fig. 5. Influence of the polyester nature on the surface energy of the glass fibres.

have a dispersive solubility parameter superior to the polar solubility parameter [19].

When an antistatic agent is applied on the fibres 13 and 15, the free surface energy and the polar component are decreased (fibres 14 and 16). An opposite result was obtained for fibres 11 and 12. This variation could be due to a more important diffusion of the antistatic agent within the sizing layer in presence of a polyester film former with a high polar character such as aromatic based polyesters.

If the hypothesis of optimised wetting properties and fibre/SMC paste adhesion properties are considered (see Section 3.1), three fibres can be selected which are the fibres 6, 11 and 16.

3.1.2. Surface properties of sized fibres after extraction

Table 4 presents the values of the free surface energy γ_s , the dispersive γ_s^D and polar γ_s^P components for the glass fibres before and after styrene extraction and for the SMC paste.

Results show that only the fibre 6 presents a good wetting behaviour and adhesion level because its free surface energy γ_{Sf} after extraction in styrene is superior to those of SMC paste γ_{Sp} and because the ratios $\gamma_{Sf}^D/\gamma_{Sp}^D$ and $\gamma_{Sf}^P/\gamma_{Sp}^P$ after extraction in styrene are close to unity. It can be supposed that the fibre 6 presents the best fibre impregnation.

3.2. Permeability measurements of glass fibre mats

A lot of researches were focused on the measurements of the permeability of glass fibre mats used for resin transfer molding (RTM) applications [20–33]. In this case, Darcy law was used and applied for a Newtonian flow:

$$\vec{v} = \frac{K}{\mu} \cdot \vec{\nabla} p, \quad (4)$$

where \vec{v} is the fluid velocity, μ the fluid viscosity, $\vec{\nabla} p$ is the pressure gradient and K the permeability second order tensor.

However, this law is available if the following hypothesis are verified:

- the resin is considered as a newtonian and incompressible fluid. In the case of SMC paste, this assumption is not verified because of the presence of additives within the SMC paste that leads to a non-Newtonian and thixotropic behaviour [31],
- the fibre mat is considered as un-deformable, which is not the case for SMC pre-pregs that can be deformed during pre-pregs process and compression moulding,
- the fibre mat is supposed to be completely impregnated by the resin. Nevertheless, during the pre-pregs manufacturing, impregnated areas remain within the sheets before moulding,
- the surface tension effects are not taken into account whereas the preliminary results presented above show that the surface properties play a major role,
- the permeability is defined as an intrinsic property of the fibre mat, supposed to be independent of the fluid nature and of the diffusion parameters. But this last one could not be considered as a negligible parameter [32,33] for SMC resin.

Moreover, the fibre orientation is defined by the mat structure for RTM applications which is not the same for SMC applications with a randomly fibre orientation. Because of all these deviations to Darcy's law, it has been chosen to develop a new experimental unit to achieve the permeability measurements which is based on the evaluation of the air flow throughout a glass fibre mat. This test looks simpler than permeability measurements based on the evaluation of the resin flow throughout the mat that needs a lot of mathematical hypothesis concerning for example the rheological behaviour of the SMC paste.

Results are given in Fig. 6 and show variations in the fibre permeability according to the sizings. Moreover, it can be observed that, no evident correlations between the permeability values and the surface properties. As a high permeability should involve a better impregna-

Table 4
Surface properties of the glass fibre sizings after extraction in styrene

Fibre	γ_{Sf} (mJ/m ²)		γ_{Sf}^D (mJ/m ²)		γ_{Sf}^P (mJ/m ²)		$\gamma_{Sf}^D/\gamma_{Sp}^D$		$\gamma_{Sf}^P/\gamma_{Sp}^P$	
	Before	After	Before	After	Before	After	Before	After	Before	After
6	30.32	26.80	19.72	20.76	10.60	6.04	0.89	0.94	8.83	5.03
7	25.81	20.81	11.41	8.89	14.40	11.92	0.52	0.40	12.00	9.93
11	28.69	18.22	20.93	4.07	7.75	14.15	0.95	0.18	6.46	11.79
14	24.74	21.59	13.53	7.24	11.21	14.35	0.61	0.33	9.34	11.95
16	30.38	18.71	17.29	10.78	13.09	7.92	0.78	0.49	10.91	6.60
SMC paste	γ_{Sp} (mJ/m ²)		γ_{Sp}^D (mJ/m ²)		γ_{Sp}^P (mJ/m ²)					
	23.30		22.10		1.20					

Before, before extraction in styrene.

After, after extraction in styrene.

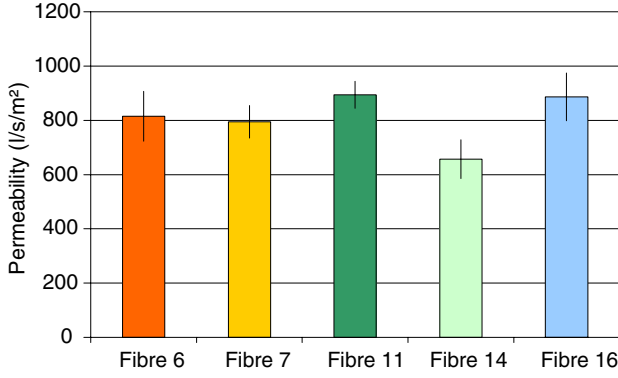


Fig. 6. Fibre permeability.

tion, fibres 11 and 16 may be accurate fibres for a good surface quality of the moulded SMC panels.

3.3. Fibre bundles stiffness

Results (Table 5) show that all the fibres have a high stiffness (around 135 mm) excepted the fibre 14 (75 mm). Nevertheless, no evident correlations can be established with the surface properties of the glass fibres.

3.4. Dielectric properties of sizing films

Two kinds of diffusion phenomena may be studied through dielectric measurements which are: (i) the swelling of the sizing by styrene and (ii) the dissolution of the sizing in styrene. In each case, the styrene is considered as the solvent and the sizing as the solute.

These two diffusion phenomena are illustrated through the measurement of the ionic conductivity as a function of time. In a first time, the increase in the ionic conductivity with time can be attributed to the sizing swelling by the styrene that lead to an increase of the styrene molecules mobility. In a second time, a decrease in the ionic conductivity with time is observed and is relative to a dissolution phenomenon where the most polar molecules of the sizing diffuse and are replaced by the less polar molecules of the styrene.

Larson et al. [34] have presented a methodology to evaluate the styrene penetration through the sizing and the dissolution coefficient of the sizing into the styrene.

Table 5
Stiffness of the glass fibres

Fibre	Stiffness (mm)
6	135
7	137
11	138
14	75
16	134

These authors proposed to measure the styrene penetration from the slope of the curve σ (ionic conductivity) versus time between t_0 , initiation of the process, and t_{\max} , time when the ionic conductivity has reached a maximum value. These authors proposed also to determine the dissolution coefficient from the relation:

$$Ds = \frac{1}{\pi} \cdot \left(\frac{2 \cdot M \cdot \Delta\sigma}{S} \right)^2, \quad (5)$$

with M the mass per area unit of the sizing film, $\Delta\sigma$ the change in ionic conductivity and S the slope of $\sigma = f(t^{-1/2})$.

For each measurement, the ratio $(\Delta\sigma/S)^2$ has been calculated, assuming that M has a constant value. Results are presented in Table 6. In agreement with Larson et al. [34] data, important standard deviations are observed. Nevertheless, a more important styrene penetration speed was observed when a fluorinated antistatic agent is applied and when an aromatic bisphenolic polyester (fibre 14) is used as film former compared to an aromatic non bisphenolic polyester (fibre 16). As concerns the dissolution phenomenon, it seems to be lowered (fibres 6, 14 and 16) or equal to zero (fibre 7), when an antistatic agent is used. This one may limit the surface treatment dissolution in the styrene. Finally it can be concluded that these two phenomena may influence the surface quality of SMC panels. Nevertheless it remains critical to establish potential chemical reactions within the sizing system because of the complexity of the formulation. It appears much more interesting to evaluate the possible correlations between the swelling and the dissolution parameters of the sizing and the surface quality of SMC panels.

3.5. Surface quality of SMC panels

SMC panels have been moulded with these three fibres to have an evaluation of their surface quality. Moreover SMC panels have been moulded with two fibres which do not present good wetting and adhesion properties which are the fibres 7 and 14 to make a comparison. After moulding, the surface aspect (Fig. 7) and the number of defects such as pinholes, bubbles, craters

Table 6
Slope A and dissolution coefficient of the glass fibre sizings

Film	Slope A (pmho min/cm)	Dissolution coefficient (cm ² /min)
6	250	1.5
7	2400 ± 220	0
11	420 ± 470	23 ± 10
14	66,000 ± 66,000	5 ± 1
16	16,000	8

When the standard deviation is not given only one measurement was performed.

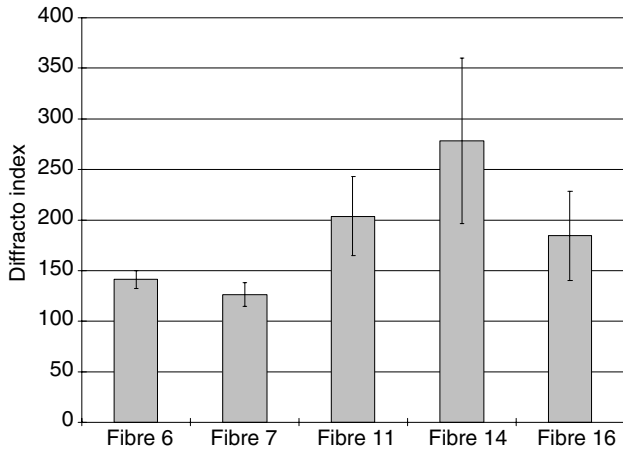


Fig. 7. Evaluation of the SMC panels surface aspect.

(Table 7) were evaluated for the fibres 6, 7, 11, 14 and 16. It can be observed, on one hand, that the best surface aspect is obtained with the fibres 6 and 7 and the worst with the fibre 14, and on the other hand, that the maximum number of defects is obtained with the fibre 14 and the minimum with the fibre 6. The SMC panels moulded with the fibres 7 and 11 are similar from the point of view of defects. The fibre 16 gives few defects except craters. As it remains difficult to establish relevant correlations between all the glass fibre characteristics and the surface quality, a statistical analysis based on PCA has been carried out.

4. Determination of correlations between the surface quality of SMC panels and the glass fibres characteristics through PCA

Based on a data matrix (Table 8), the PCA statistical analysis consists firstly in a graphical representation showing the potential relationships existing between the glass fibres characteristics and the surface quality by means of two concentric circles around a gravity center with $r = 0.7$ and 1 ($r =$ circle radius). This radius corresponds to the correlation coefficient value assimilated to the cosine angle. The significant parameters are located between these two circles. Then this statistical analysis consists in the determination of the correlations existing between the different parameters from the angle value. These correlations are the followings: (i) two

parameters are positively correlated if they form angles less than 90° , (ii) two parameters are independent if they form an angle of 90° and (iii) two parameters are negatively correlated if they form angles more than 90° .

For this study, three kinds of PCA have been provided: (i) between the glass fibre characteristics and the surface quality (Table 9), (ii) between the glass fibre characteristics themselves (Table 10) and (iii) between the surface quality and the material flow (Table 11).

As it can be observed on Fig. 8 all the parameters can be taken into account with the exception of the polar ratio before styrene extraction of the sizing which is not located between the two concentric circles.

A positive correlation indicates that when one of the glass fibres characteristics increases, one of the surface quality parameters increases. In the case of a negative correlation, one of the surface quality parameters decreases when one of the glass fibres characteristics increases.

4.1. Correlations between the glass fibre characteristics and the surface quality

Table 7 gives the correlations obtained between the glass fibres characteristics and the surface quality of the SMC panels (Diffraction index and defect numbers).

Results show that the permeability of the glass fibres presents a significant negative correlation with the number of defects such as pinholes and bubbles. The higher the permeability, the more numerous the defects. On the face of correlation coefficients, the permeability may be less correlated to the Diffraction index and the crater number.

The styrene solubility is slightly positively correlated with the surface quality of SMC panels, because of low correlation coefficients. Nevertheless, the pinholes number could be increased when a high styrene solubility is obtained (correlation coefficient: 0.765). Thus, it might be necessary to perform sizings with low solubility in styrene.

The fibre stiffness appears to be one of the most important characteristics that should be considered in the optimisation of the surface quality. The negative correlation coefficients are high whatever the type of defects and indicate that the glass fibre sizing must give a good stiffness to get fewer defects and a low Diffraction index.

Table 7
Defects number

	Fibre				
	6	7	11	14	16
Pinhole number	0.7 ± 0.8	1.0 ± 1.3	0.7 ± 1.2	7.5 ± 4.7	0
Bubble number	0	0.2 ± 0.4	0.2 ± 0.4	2.5 ± 2.3	1.2 ± 1.5
Crater number	5.2 ± 4.0	8.0 ± 7.0	8.3 ± 7.5	11.7 ± 4.5	10.3 ± 10.6

Table 8
Data matrix of PAC

	Fibre				
	6	7	11	14	16
Diffraeto index	141	126	204	278	184
Pinhole number	0.67	1	0.67	7.5	0
Bubble number	0	0.17	0.17	2.5	1.17
Crater number	5.17	8	8.33	11.67	10.33
Stiffness (mm)	135	137	138	75	134
Permeability (l/s/m ²)	815	795	894	657	887
Styrene solubility (%)	56	61	46	67	45
Surface energy (γ_s) (mJ/m ²)					
Before	30.32	25.81	28.69	24.74	30.39
After	26.80	20.81	18.22	21.59	18.71
Dispersive ratio ($\gamma_{Sf}^D/\gamma_{Sp}^D$)					
Before	0.89	0.52	0.95	0.61	0.78
After	0.94	0.40	0.18	0.33	0.49
Polar ratio ($\gamma_{Sf}^P/\gamma_{Sp}^P$)					
Before	8.83	12.00	6.46	9.34	10.91
After	5.03	9.93	11.79	11.95	6.60
Swelling (pmho min/cm)	250	2400	420	66000	16000
Dissolution (cm ² /min)	1.5	0	23	5	8

Before, before styrene extraction.
After, after styrene extraction.

Table 9
Correlation matrix between the glass fibre characteristics and the surface quality

	Diffraeto index	Pinholes	Bubbles	Craters
Permeability	-0.524	-0.922	-0.690	-0.387
Styrene solubility	0.244	0.765	0.443	0.157
Stiffness	-0.846	-0.987	-0.914	-0.672
Surface energy (γ_s) (mJ/m ²)				
Before	-0.425	-0.758	-0.507	-0.493
After	-0.294	0.095	-0.181	-0.628
Dispersive ratio ($\gamma_{Sf}^D/\gamma_{Sp}^D$)				
Before	-0.042	-0.463	-0.415	-0.428
After	-0.509	-0.274	-0.313	-0.663
Polar ratio ($\gamma_{Sf}^P/\gamma_{Sp}^P$)				
Before	-0.378	-0.048	0.126	0.170
After	0.600	0.558	0.377	0.556
Swelling	0.864	0.942	0.975	0.786
Dissolution	0.347	-0.173	-0.111	0.154

Before, before extraction in styrene.
After, after extraction in styrene.

This observation is in agreement with Dana et al. conclusions [37]. In fact, these authors have shown that to obtain a good surface aspect, an uniform glass fibre distribution in the mould to allow the fibres to flow with the resin is necessary. Hence, this flow ability is directly bound with the fibre stiffness which is undoubtedly monitored by the sizing chemistry. But it is important to notify that the stiffness have been determined before the impregnation. Further investigations should be carried on to evaluate the stiffness variations after the impregnation.

Regarding the glass fibre surface properties, different kinds of correlation can be given in evidence. It can be observed that the wettability of the glass fibre before

extraction is negatively correlated (-0.758) with the pinholes number. Mellian [35] has reported similar results for the bubbles number which is increased for glass fibres with low wettability by the SMC paste. From these results, it can be suggested to favour fibres with high free surface energy for a better surface quality of moulded parts [36]. Nevertheless this correlation does not seem to be verified once the sizing is solubilized by styrene excepted for the craters number (correlation coefficient: -0.628).

The swelling of the glass fibre sizings is strongly positively correlated with the surface quality of SMC panels. Also, the more important the swelling, the greater the Diffraeto index and the greater the number of defects.

Table 10
Correlation matrix between the glass fibre characteristics

	Permeability	Styrene solubility	Stiffness	Surface energy (γ_s) before	Surface energy (γ_s) after	Dispersive ratio before ($\gamma_{st}^D/\gamma_{sp}^D$)	Polar ratio before ($\gamma_{st}^P/\gamma_{sp}^P$)	Dispersive ratio after ($\gamma_{st}^D/\gamma_{sp}^D$)	Polar ratio after ($\gamma_{st}^P/\gamma_{sp}^P$)	Swelling	Dissolution
Permeability	1										
Styrene solubility	-0.946	1									
Stiffness	0.889	-0.697	1								
Surface energy (γ_s) before	0.789	-0.810	0.670	1							
Surface energy (γ_s) after	0.459	0.129	0.670	0.789	1						
Dispersive ratio before ($\gamma_{st}^D/\gamma_{sp}^D$)	0.640	0.060	0.427	0.789	0.060	1					
Polar ratio before ($\gamma_{st}^P/\gamma_{sp}^P$)	-0.201	0.318	0.020	-0.238	0.026	-0.784	1				
Dispersive ratio after ($\gamma_{st}^D/\gamma_{sp}^D$)	0.018	0.071	0.231	0.519	0.071	0.211	0.182	1			
Polar ratio after ($\gamma_{st}^P/\gamma_{sp}^P$)	-0.365	0.303	-0.473	-0.762	-0.558	-0.278	-0.894	-0.278	1		
Swelling	-0.819	-0.980	-0.980	-0.617	-0.448	-0.448	-0.276	-0.276	0.438	1	
Dissolution	0.512	0.180	0.180	0.236	-0.628	0.648	-0.779	0.608	0.449	-0.164	1

Before, before extraction in styrene.
After, after extraction in styrene.

Therefore the sizing swelling by styrene might be lowered to avoid the formation of voids at the fibre/SMC paste interface and to obtain a good surface quality.

On the contrary, the dissolution parameter is slightly positively correlated with the Diffracto index and the defects number, the value angles being near 90° .

4.2. Correlations between the glass fibre characteristics

Table 10 gives informations on the relationships which should exist between the various glass fibre characteristics themselves.

The glass mat permeability can give indications on the wet-through phenomenon which is related to the sizing solubility in the styrene and to the stiffness. In fact a highly soluble sizing in styrene and few stiff fibres should decrease the wet-through phenomenon [37]. Hence, it is attempted that the solubility is inversely proportional to the stiffness. This result is in good agreement with PCA data because correlation coefficients of -0.946 and 0.889 , respectively, between the styrene solubility and the permeability and between the fibre stiffness and the permeability were obtained. Moreover, a negative correlation between the sizing styrene solubility and the glass fibre mat permeability has been obviously observed (correlation coefficient = -0.697).

The swelling and dissolution parameters seem to be independent factors (correlation coefficient: -0.164). It can be noticed that the swelling phenomenon is strongly negatively correlated with the stiffness (correlation coefficient: -0.980). In fact the sizing swelling may decrease the network density and thus gives a low stiffness [37]. Moreover, the glass mat permeability is minimized (correlation coefficient: -0.819) at the opposite of the dissolution phenomenon.

4.3. Correlations between the surface quality and the material flow

During the moulding phase, the deformation work (W_{def}) relative to the energy dissipated during the material flow was evaluated. Indeed, this deformation work may improve the understanding of the apparition of the defects on SMC panels.

To understand the correlations that may exist between the deformation work and the surface aspect, the statistical analysis has been carried on by taking into account the glass fibre characteristics (Table 11).

Results show that the Diffracto index has a negative correlation with the deformation work (correlation coefficient = -0.859). This last data is relative to the flow of the material during the moulding, indicating that the higher the viscosity (W_{def} important), the better the surface aspect.

Nevertheless, the deformation work seems to be correlated to the surface defects. The negative coefficients

Table 11
Matrix correlation between the glass fibre characteristics, the deformation work and the surface quality

	Diffracto index	Pinholes	Bubbles	Craters	Permeability	Styrene solubility	Stiffness	Surface energy (γ_s) before	Surface energy (γ_s) after	Surface energy (γ_s) after	Dispersive ratio before ($\gamma_{St}^D/\gamma_{Sp}^D$)	Polar ratio before ($\gamma_{St}^P/\gamma_{Sp}^P$)	Dispersive ratio after ($\gamma_{St}^D/\gamma_{Sp}^D$)	Polar ratio after ($\gamma_{St}^P/\gamma_{Sp}^P$)	Swelling	Dissolution
W_{def}	-0.859	-0.810	-0.975	-0.952	0.626	-0.391	0.863	0.584	0.372	0.473	-0.144	0.503	-0.522	-0.937	0.008	

Before, before styrene extraction.
After, after styrene extraction.

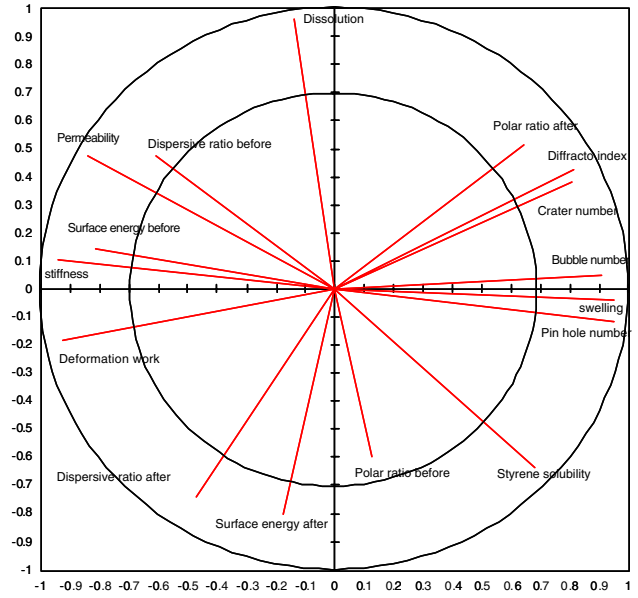


Fig. 8. Principal component analysis.

give evidence that a high viscosity might minimise the apparition of the surface defects on SMC panels.

Finally, the values of the correlation coefficients between the different glass fibres characteristics and the deformation work give evidence that these coefficients are significant in the case of the stiffness (0.863), the permeability (0.626) and the swelling (-0.937). Consequently, a high fibre stiffness, a high permeability of the mat fibres and a low swelling of the fibre sizing should increase deformation work and thus the surface quality of the moulded SMC panels.

5. Conclusions

The purpose of this study was to get a better understanding of the relationships between the glass fibre characteristics, the material flow and the surface quality of the SMC panels according to the sizing composition of the glass fibre.

One of the main difficulties to interpret the results was the glass fibre characteristics are dependent on each others and particularly the fibre stiffness, the glass mat permeability and the sizing solubility and swelling. But, a global analysis allowed to conclude that these three factors are the most important ones so that: (i) a better surface quality may be obtained if the glass fibre mat permeability is important (around $9001 \text{ s}^{-1} \text{ m}^{-2}$), (ii) a high fibre stiffness before impregnation (around 135 mm) should improve the glass fibre distribution during the moulding, (iii) a low styrene solubility of the sizing (around 50%) should decrease the defect formation and (iv) a low swelling of the surface treatment should be required.

The study also showed that the deformation work was correlated to the surface quality of the moulded SMC panels so that a good surface quality could be obtained for highly viscous resin (important W_{def}) which is the case for glass fibres having a high stiffness, a high permeability of the fibre mat and a low swelling of the fibre sizing.

Finally, this work has emphasized the statistical analysis based on PCA to determine the key parameters related to glass fibres and moulding conditions that may influence the surface quality of SMC panels.

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References

- [1] Al Moussawi H, Drown EK, Dzral LT. The silane/sizing composite interphase. *Polym Compos* 1993;14(3):195–200.
- [2] Tsutsumi K, Ohsuga T. Surface characterization of modified glass fibres by inverse chromatography. *Coll Polym Sci* 1990;268:38–44.
- [3] Barraza HJ, Hwa MJ, Blakey K, O'Rear EA, Grady BP. Wetting behavior of elastomer-modified glass fibers. *Langmuir* 2001;17:5288–96.
- [4] Park S-J, Kim T-J. Studies on surface energetics of glass fabrics in an unsaturated polyester matrix system: effect of sizing treatment on glass fabrics. *J Appl Polym Sci* 2001;80:1439–45.
- [5] Gao P, Su KB, Ward Y, Weng LT. Effects of chemical composition and thermal stability of finishes on the compatibility between glass fiber and high melting temperature thermoplastics. *Polym Compos* 2000;21(2):312–21.
- [6] Thomason JL. The interface region in glass fibre-reinforced epoxy resin composites: 3. Characterization of fibre surface coatings and the interphase. *Composites* 1995;26(7):487–98.
- [7] Larson BK, Dzral LT. Glass fibre sizing/matrix interphase formation in liquid composite moulding: effects on fibre/matrix adhesion and mechanical properties. *Composites* 1994;25(7):711–21.
- [8] Thomason JL. The interface region in glass-reinforced epoxy resin composites: 1. Sample preparation, void content and interfacial strength. *Composites* 1995;26(7):467–75.
- [9] Drown EK, Al Moussawi H, Dzral LT. Glass fiber sizings and their role in fiber-matrix adhesion. *J Adhesion Sci Technol* 1991;5(10):865–81.
- [10] Palmese GR, Andersen OA, Karbhari VM. Effect of glass fiber sizing on the cure kinetics of vinyl-ester resins. *Composites: Part A* 1999;30:11–8.
- [11] Gorowara RL, Kosik WE, McKnight SC, McCullough RL. Molecular characterization of glass fiber surface coatings for thermosetting polymer matrix/glass fiber composites. *Composites: Part A* 2001;32:323–9.
- [12] Feuillade V. Etude de l'influence de la formulation de l'ensimage des fibres de verre sur la qualité de surface des composites SMC de type "classe A". PhD Thesis. Montpellier, France; 2003.
- [13] Norme ISO 11667: 1997, Plastiques renforcés de fibre – Préimprégnés et compositions de moulage – Détermination des taux de résine, de fibre de renfort et de charge minérale – Méthodes par dissolution; 1997.
- [14] Ollive C. Critères de choix et avenir des SMC dans l'automobile. *Composites* 1991(3):145–52.
- [15] Owens DK, Wendt RC. Estimation of the surface free energy of polymers. *J Appl Polym Sci* 1969;13:1741–7.
- [16] Gonzalez-Benito J, Baselga J, Aznar AJ. Microstructural and wettability study of surface pretreated glass fibres. *J Mater Process Technol* 1999;92–93:129–34.
- [17] Brandrup J, Immergut EH. editors. *Polymer handbook*. 3rd ed., Section V, Physical constants of some important polymers; 1989. p. 73.
- [18] Brandrup J, Immergut EH. editors. *Polymer handbook*. 3rd ed., Section VI, Surface and interfacial tensions of polymers, oligomers, plasticizers, and organic pigments; 1989. p. 425.
- [19] Brandrup J, Immergut EH. editors. *Polymer handbook*. 3rd ed., Section VII Solubility parameters values; 1989. p. 540–42.
- [20] Parnas RS, Howard JG, Luce TL, Advani SG. Permeability characterization. Part 1: A proposed standard reference fabric for permeability. *Polym Compos* 1995;16(6):429–45.
- [21] Sheard J, Senft V, Mantell SC, Vogel JH. Determination of corner edge permeability in Resin Transfer Molding. *Polym Compos* 1998;19(1):96–105.
- [22] Berker B, Sun JQ. Adaptive control and on-line permeability estimation of Resin Transfer Molding for composites materials. *J Mater Process Manufact Sci* 1998;6:193–203.
- [23] Parnas RS, Flynn KM, Dal-Favero ME. A permeability database for composites manufacturing. *Polym Compos* 1997;18(5):623–33.
- [24] Weitzenböck JR, Sheno RA, Wilson PA. Radial flow permeability measurement. Part A: Theory. *Composites: Part A* 1999;30:781–96.
- [25] Weitzenböck JR, Sheno RA, Wilson PA. Radial flow permeability measurement. Part A: Application. *Composites: Part A* 1999;30:797–813.
- [26] Lundström TS, Gebart BR, Sandlund E. In-plane measurements on fiber reinforcements by the multi-cavity parallel flow technique. *Polym Compos* 1999;20(1):146–54.
- [27] Weitzenböck JR, Sheno RA, Wilson PA. Measurement of principal permeability with the channel flow experiment. *Polym Compos* 1998;20(2):321–35.
- [28] Parnas RS, Salem AJ, Sadiq TAK, Wang H-P, Advani SG. The interaction between micro- and macroscopic flow in RTM preforms. *Compos Struct* 1994;27:93–107.
- [29] Kim SK, Daniel IM. Determination of three-dimensional permeability of fiber preforms by the inverse parameter estimation technique. *Composites Part A: Appl Sci Manufact* 2003;34(5):421–9.
- [30] Buntain MJ, Bickerton S. Compression flow permeability measurement: a continuous technique. *Composites Part A: Appl Sci Manufact* 2003;34(5):445–57.
- [31] Collister J, Allen P. Sheet molding compound rheology. In: Kia HG. editor. *SMC sheet molding compounds science and technology*; 1993. p. 139.
- [32] Karbhari VM, Palmese GR. Sizing related kinetics and flow considerations in the resin infusion of composites. *J Mater Sci* 1997;32:5761–74.
- [33] Ahn KJ, Seferis JC, Berg JC. Simultaneous measurements of permeability and capillary pressure of thermosetting matrices in woven fabric reinforcements. *Polym Compos* 1991; 12(3):146–52.

- [34] Larson BK, Dzral LT, Van Antwerp J. Swelling and dissolution rates of glass fiber sizings in matrix resin via micro-dielectrometry. *Polym Compos* 1995;16(5):415–20.
- [35] Mellian W. Troubleshooting thought process. In: Kia Hamid G. editor. *Sheet molding compounds science and technology*; 1993. p. 209–10 [chapter 11].
- [36] Mellian W. Troubleshooting thought process. In: Kia Hamid G. editor. *Sheet molding compounds science and technology*; 1993. p. 196–7 [chapter 11].
- [37] Dana DE, Yu JF. Sheet molding compound glass fibers. In: Kia Hamid G. editor. *Sheet molding compounds science and technology*; 1993 [chapter 7].