Effect of glass fiber sizing on Sheet Molding Compounds (SMC) rheology

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ABSTRACT

The influence of the sizing on the bundles mechanical characteristics and sheet molding compound rheology are investigated in this study. Two glass fiber sizing formulations are considered, one containing PVAc and the other polyester/PVAc, used in SMC materials. Axial compression tests are conducted on dry 2D random suspensions. The bending rigidity of the fiber bundles are predicted through a modified theoretical model. This value is found to depend on the bundle sizing as well as on the interaction with solvents present in the SMC paste. Molding experiments are performed on planar SMC sheets using the two different fiber bundles as reinforcements. The results confirm the dependence of the molding energy and the SMC rheology on the bundles chemical and mechanical characteristics.

1.INTRODUCTION

SMC are highly concentrated suspensions of particles and glass bundles suspended in a thermosetting resin, in most cases unsaturated polyester. The glass reinforcement is under the form of bundles which are one unit segments consisted of an assembly of hundreds glass fibers of cylindrical shape and circular cross section of 15 μm in average. These filaments or fibers are highly cohesive thanks to a sizing which is a hybrid organic-inorganic " coating" applied to the glass filaments. The resulting bundle has a high degree of integrity throughout the SMC process. It is rather slender, cylindrical, with an elliptical cross section defined with a minor axis (c) around 100 μm and a major axis (b) around 800μm.

The sizing layer consists of a film forming polymer, such as unsaturated polyesters or polyvinyl acetates and also incorporates lubricants, surfactants, coupling and anti static agents [1]. It is designed to protect the glass bundles during subsequent processing and to provide optimum bundle impregnation in the resin by enhancing the intrinsic properties and chemical potential of the formed bundle [2, 3].

In this study, bundle-bundle and bundle-matrix interaction are investigated in order to correlate the glass fibres sizing formulation, the bundle stiffness and the compound rheology. The possibility of determining the bending rigidity of each bundle when subjected to bending deformation conditions as well as the correlation between this value and the behaviour of the impregnated layer will improve our understanding of the governing physical phenomena and therefore lead to a better control of the process and the final composite.

2. MATERIALS AND EXPERIMENTS

a. Materials

Two different commercial bundles, F1 and F2, are tested both having a sizing composed mainly of polyvinyl acetate (PVAc) with addition of polyester for bundle F2. The cross section dimensions of each bundle is determined thanks to optical and scanning electron microscopy. The suspending medium consists of a standard paste used for SMC moulding containing PVAc as a Low Profile additive and an unsaturated polyester resin both provided by Dow automotive. The exact formulation is not given here, but it may be noted that such compounds generally contain in addition a calcium carbonate filler and magnesium oxide as a thickening agent. Inhibitors and reaction initiators are used in order to control the cure time.

b. Packing stress

To determine the stiffness of a bundle, axial compression experiments are conducted first on dry bundle beds. The experimental set-up used consists of two parallel plates of $150\times150mm^2$ mounted on a hydraulic press with a 100 kN load cell (Fig.1). A layer of $1kg/m^2$ dispersed bundles is prepared for each reinforcement type. This value is chosen according to the glass fibre density in a SMC production line.

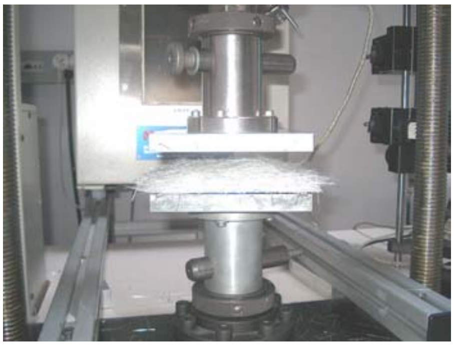

Fig. 1Compression device of dry bundles

The styrene present in the organic phase of the SMC paste will be the major reactive ingredient with the sizing before moulding [4]. Therefore, in order to determine how the chemical interactions between the resin and the sizing will affect the characteristics of the bundles, mainly their stiffness, the bundles are soaked in styrene for six hours, time after which no additional dissolution of the sizing has been observed [5]. The styrene is then evaporated completely without disturbing the bundles spatial distribution. The compression experiments are then conducted.

c. Compression tests of SMC layers

Compression experiments are performed on SMC compounds in order to correlate the bundle stiffness to flow resistance and molding rheology. The samples are square SMC sheets containing about 25% bundles in volume and manufactured with an industrial compounding machine. The temperature and the pressure are carefully registered during the flow. The tests are conducted with a constant surface condition, i.e., the SMC sheets have the same surface as the open mould. A constant pressure is thus always applied during moulding and the suspension flows out of the mould. It aims to characterise the bending of bundles under axial compression in a lubricated medium. The time evolution of the gap is measured for both bundle types at the same moulding pressure. The experiment is isothermal (T=70°C) with a constant squeezing velocity condition(v= 0.1 mm/min). The material used for this experiment is model SMC which did not include the initiator so the curing reaction would be delayed.

3. ANALYTICAL MODELING OF THE PACKING STRESS

Fiber bundle rigidity is analysed through packing stress modelling of fiber bundles network. In the following only the forced packing regime is studied. Power laws describe generally well the relationship between the packing stress and the fiber volume fraction: $P = k\Phi^n$, where k is proportional to the bundle rigidity, orientation and cross section and n to the number of contact points between the bundles. The power law index was found to be 3 for 3D fiber networks [6] and more than 7 for unidirectional fiber beds and woven structures [7]. The analytical expression of the packing stress is obtained through a modified approach of Toll's [7] model for fiber packing. This modified version is specially adapted for SMC bundles and expresses the packing stress as a function of the number of deformation units per unit volume μ, the volume fraction of the fiber bundles Φ and the compliance of each deformation unit $\bar{s}$ [8].

$$P = c^2 \int_0^{\Phi} \frac{\mu}{\Phi \bar{s}} d\Phi = \frac{2}{5}\frac{8^4}{\pi^5} f^4 \frac{c}{b^5} B\Phi^5 \qquad \text{(eq. 1)}$$

where B is the fiber bundle bending rigidity, f is the orientation function, c and b the minor and major axis of the bundles cross section respectively.

4. RESULTS & DISCUSSION

a. Packing stress

Fig. 2 plots the experimental packing stress curves versus the bundles volume fraction for both bundles F1 and F2. The compression test on styrene soaked bundles is presented alongside on the graph with suffixes"-s". The consequence of the interaction with styrene on the bundle is a general decrease in its bending rigidity. These changes are denoted by the decrease in the exponent as well as by the decrease in the slope of the curves in the logarithmic scale. All experimental curves are fitted with a power law of the bundles volume fraction with an exponent around 4.4 for dry bundles and 3.9 for styrene soaked bundles. The value of the exponent expected by the model is 5 for 2D random spatial distribution of the dispersed bundles. The dry suspensions thus behave quite closely to a 2D random mat. However for styrene soaked bundles, the decrease in the exponent reveals a significant change in the number of contact points between the fiber bundles probably due to slight local orientation induced by remaining styrene or the dissociation of the bundles, weakened by the partial dissolution of the sizing in the styrene, into unit fibers.
The bundle rigidity is estimated using eq.1. The results are summarized in table1 with the values of the estimated rigidity for dry bundles, styrene soaked bundles and the relative rigidity loss.

Bundle	$B_d(10^{-5}N.m^2)$	$B_s(10^{-5}N.m^2)$	ΔB/B%
F1	**1.47**	**0.447**	**↘67**
F2	**3.04**	**0.867**	**↘71**

Table 1 Summary of bundles rigidity estimated with the eq.1

The presence of polyester components in the sizing thus seems to enhance the rigidity of the bundle since bundle F2 exhibits a higher stiffness than F1. On the other hand, the bending rigidity of the bundles soaked in styrene is decreased by about 70% in both cases. F2-s remains slightly stiffer than F1-s. More investigations are needed in order to validate the use of this analytical approach in the modelling of the bending rigidity of rather soft fiber bundles.

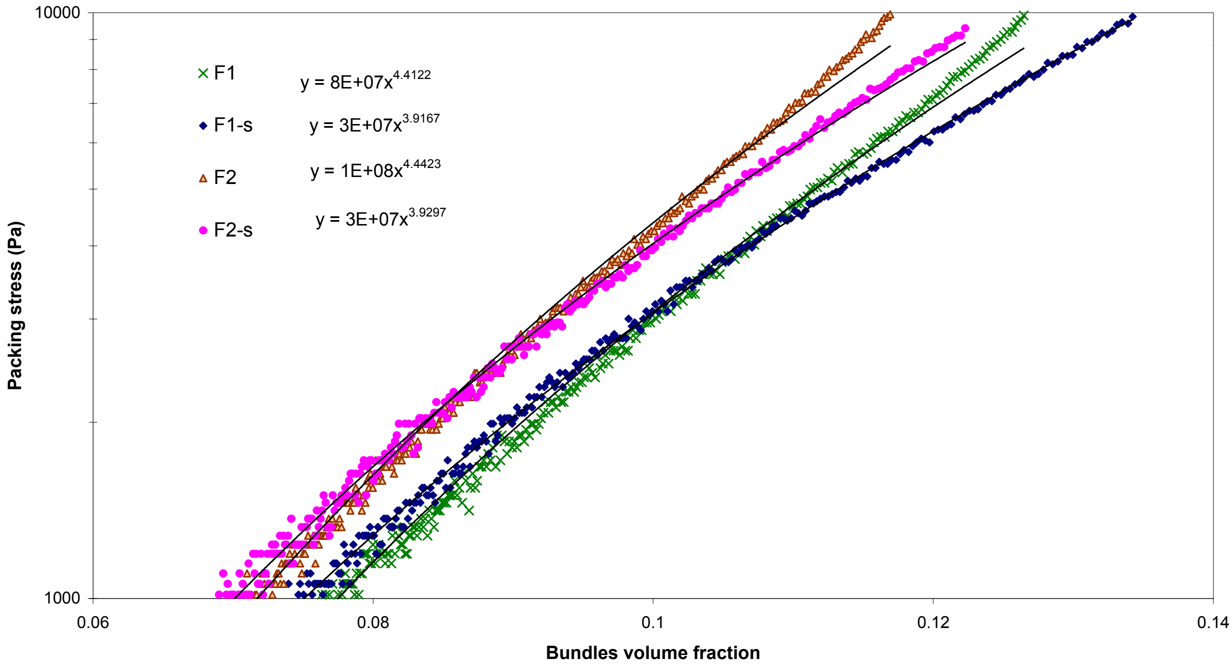

Fig. 2 Experimental data (dots) and fit(-) of the packing stress versus bundles volume fraction for dry (F1, F2) and styrene soaked (F1-s, F2-s) fiber bundles

b. Constant surface experiment : bending and flow in a lubricated medium

The Fig. 3 shows the pressure versus strain during isothermal compression tests for SMC with two reinforcements types. The behaviour of both SMC compounds is quite similar: first an initially flat part of the curve is commonly attributed to void squeezing which is strain independent, then the stress increases rapidly with strain denoting an increase of the material

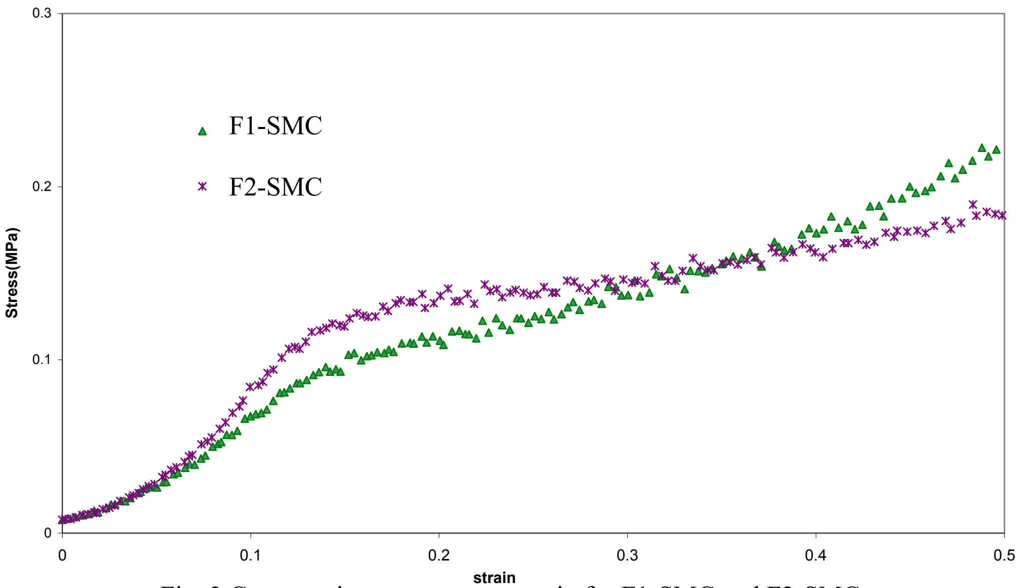

Fig. 3 Compression stress versus strain for F1-SMC and F2-SMC

stiffness with deformation [9]. The SMC sheet with a F2 reinforcement type shows a higher resistance to the flow at the beginning of the compression (strain ~ 0.12) likely because of normal solicitation of the bundles through bending deformation. This is in agreement with the experiments on dry bundles suspensions that revealed a higher stiffness for bundle F2 in forced packing deformation. Polyester based bundles sizing thus contributes to an increase of the composite stiffness and flow resistance at the beginning of the compression. At this stage no flow is observed out of the mold. This step is followed by a change in the curve slope marked by a yield effect which is probably associated to the break-down of the gel network induced by the thickening agent [10]. This yield effect depends upon the bonds strength and therefore upon the sizing–matrix interaction. Lower flow resistance is then observed with SMC with F2 bundles than SMC with F1 bundles which exhibits a significant increase of the pressure with the strain.

Research is currently being done in order to correlate the bending deformation to the flow rheology. Experiments are preformed using a mold specially designed for SMC plates production. The first results are in good agreement with the previous observations and will be presented in a future publication.

4.CONCLUSIONS

In this study we focused on the effect of using a polyester component in the sizing formulation on the bending rigidity of glass fiber bundles used for SMC compounds and the resulting rheological behaviour. It is confirmed that the bundle sizing exerts a large influence on the rheology of SMC and on the bundles mechanical characteristics. The compression of SMC sheets as well as the packing stress measurements on dry bundles suspension revealed that the use of a polyester component in the sizing enhances the rigidity of the bundles and guarantees a higher integrity after the interaction with the solvent present in the SMC paste.

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References

1. **Vetrotex Saint-Gobain** europeen centre of tests and reaserch , “ Verre textile pour renforcement des matières plastiques”, *Les cahiers du Plastique Armé*, **7714**, (1978), 51

2. **Thomason, J.L.** and **Adzima , L.J.**, “Sizing up the interphase : an insider’s guide to the science of sizing”, *Composites: Part A*, (2001), 313-321

3 **Thomason, J.L.**, “The interface region in glass fibre-reinforced epoxy resin composites: 3. Characterization of fibre surface coatings and the interphase”, *Composites*, **26**/7, (1995), 487-498

4. **Dibenedetto, A.T., Connelly, S.M., Lee, W.C., Accorsi, M.L.**, “The properties of organosiloxane/polyester interfaces at an E-glass fiber surface”, J. of Adhesion, **52**, (1995), 41-64

5. **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, University of MontpellierII*, Dec. 2003

6 **Van Wyk, C.M.**, “Note on the compressibility of wool”, *J. Textile Intitute*, **37**, (1946), 285-292

7 **Toll, S**., “ Packing mechanics of fiber reinforcements ”, *Polym. Eng. and Sci.*, **38**/8, (1998), 1337- 1350

8 **Merhi, D., Comte, E., Michaud, V., Månson, J.A.-E**., “Predicting bending rigidity of glass fiber bundles in sheet molding compounds”, *to be submitted to Composites A*.

9 **Silva-Nieto, R.J., Fisher, B.C.** and **Birley A.W.,** "Rheological characterization of unsaturated Polyester resin sheet molding compund", Polymer Eng. Sc., **21**/8, (1981), 499-506

10 **Kotsikos G.** and **Gibson A.G.**, "Investigation of the squeeze flow behaviour of sheet moulding compounds(SMC)", Composites Part A, **29A**, (1998), 1569-1577