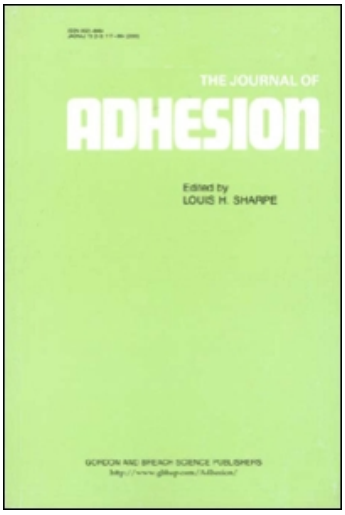


**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

# Tool Preparation in Autoclave Manufacturing of Thermoset Matrix Composites and its Relevance to Adhesion

Q. Bénard[a]; M. Fois[a]; M. Grisel[a]
[a] Unité de Recherche en Chimie Organique et Macromoléculaire, Université du Havre, Le Havre cedex, France

**To cite this Article** Bénard, Q. , Fois, M. and Grisel, M.(2007) 'Tool Preparation in Autoclave Manufacturing of Thermoset Matrix Composites and its Relevance to Adhesion', The Journal of Adhesion, 83: 11, 987 — 1001
**To link to this Article: DOI:** 10.1080/00218460701751889
**URL:** http://dx.doi.org/10.1080/00218460701751889

*The Journal of Adhesion*, 83:987–1001, 2007

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460701751889

Taylor & Francis
Taylor & Francis Group

# Tool Preparation in Autoclave Manufacturing of Thermoset Matrix Composites and its Relevance to Adhesion

**Q. Bénard**
**M. Fois**
**M. Grisel**
Unité de Recherche en Chimie Organique et Macromoléculaire, Université du Havre, Le Havre cedex, France



*The choice of a manufacturing process is of primary importance to control composite materials properties and optimize their performance. Moreover, various parameters of a given implementation may also modify these properties in a significant way. Hence, this paper aims to underline the role of tool preparations in an autoclave process of composite manufacturing and their different links with adhesion performance. To this purpose, the influence of surface characteristics is discussed in terms of wettability, roughness, and by microscopy and chemical analysis. A link between the surface properties and adhesion performance has been assessed* via *single lap shear tests. Results clearly demonstrate the major influence of surface contamination and roughness but also the role of fibre reinforcement on adhesion properties.*

**Keywords:** Adhesion; Autoclave process; Destructive tests; Surface analysis; Surface properties

## 1. INTRODUCTION

From a general point of view, manufacturing of composite materials always needs to be designed depending on the application; in all cases, the composite properties are mainly related to both implementation and materials used. Nevertheless, variations in manufacturing process parameters may also significantly influence the material surface

Received 20 June 2006; in final form 20 September 2007.
Address correspondence to Michel Grisel, Unité de Recherche en Chimie Organique et Macromoléculaire, URCOM, EA 3221, Université du Havre, 25 Rue Philippe Lebon, B.P. 540, F-76058 Le Havre cedex, France. E-mail: michel.grisel@univ-lehavre.fr

properties such as printability, surface characteristics or wear behaviour [1–3]. As an example, Twigg *et al.* [4] have analysed tool-part interaction in an autoclave process in order to understand its influence on warpage of the part. Fung [5] proceeded to the optimisation of injection moulding process parameters to reach good wear properties.

In addition to that, as adhesion abilities are governed by numerous parameters [6] such as roughness [7], surface free energy [8], chemical composition [9], and many others, it clearly appears that great care has to be taken during the manufacturing process of the composite surface in order to obtain satisfactory material properties.

The present study aims to bring an original understanding of the effect of tool preparation in an autoclave process on adhesion properties of the resulting surfaces.

When taking into account all phenomena governing adhesion, it is of interest to point out the influence of the manufacturing process on the surface aspect prior to any additional surface treatment. It is important to underline that most of the studies, done on surface treatment do not consider the tool preparation as a surface treatment [4–10], but often consider the resulting surface as a homogeneous bare surface whatever the surface preparation steps used. Through the present experimental data it is clearly demonstrated that tool preparation can affect and greatly modify surface parameters in such a way that it has to be considered as a real and efficient surface treatment.



## 2. MATERIALS AND METHODS

### 2.1. Composite Materials

Carbon/epoxy and glass/epoxy composites were manufactured by AIRCELLE (SAFRAN Group, Le Havre, FRANCE) using an autoclave process. Samples were cured for 1 h at 180°C under 7.5 bars pressure, and then post-cured for 4 h at 190°C with no pressure. The epoxy thermoset resin remains exactly the same for both composites, only the fibre reinforcement (glass and carbon, oriented at 0°) being different from one composite to another. Hence, both glass and carbon fibres are sized to ensure a good fibre matrix interface with a silane and an epoxy coupling agent, respectively. Ten pre-impregnates are superimposed to obtain the glass/epoxy material while only eight pre-impregnates are used for the carbon/epoxy one. Pre-impregnate plies (approximately 0.2 mm thick) were superposed against different tool preparations as described in the next paragraph. At the end of the curing cycle, the thickness of both carbon and glass/epoxy sample

composites is about 2 mm. Due to the high performance expected for aeronautic applications, the average fibre volume of the corresponding composite materials is above 60%.

## 2.2. Tool Preparations

Materials were prepared as depicted on Figure 1, with mainly three different tool (aluminium) preparations described below:

A. The first is a fluorinated film release cloth (0.3 μm thick) which induces a smooth and reflecting aspect to the composite surface.
B. The second one is a non-porous Teflon® ply (0.7 μm thick) which induces a rougher surface, corresponding to the ply imprint.
C. The third one is a silicone mould release agent called Frekote® 44 NC (Loctite, Seulis, France) that is spread and cured onto the tool surface prior to manufacturing the composite.

Moreover, two additional tool preparations were used in the present study:

D. One was prepared with a Teflon ply which was recovered with the fluorinated film in order to confer on it a rough aspect, keeping the fluorinated film's effect on the composite surface.
E. The last tool preparation is linked to the pre-impregnate stacking, prior to the cure step. The stacking of several pre-impregnates is done with an additional non impregnate ply (carbon or glass woven with the same characteristics as those of the composite) placed at the bottom of the composite stack (meaning at the composite surface), directly on the Frekoted tool. For this last preparation, polymer absorption was done in order to maintain the 60% fibre

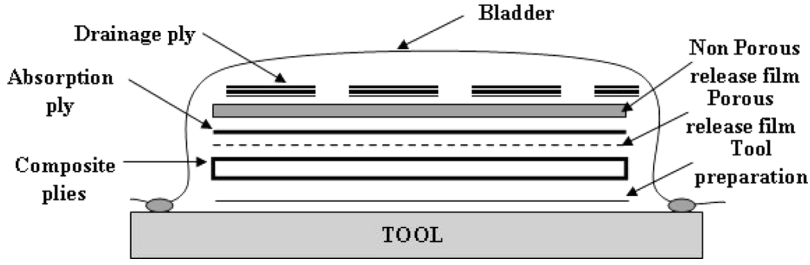


**FIGURE 1** Schematic stacking in autoclave process.

content; indeed, this non impregnate additional ply absorbs an important amount of epoxy matrix. This sample will be called Frekote + dry ply.

In the following discussion, the five distinct tool preparations are denoted A, B, C, D, and E in order to keep the discussion as clear as possible.

## 2.3. Contact Angle Measurements

The contact angle of sessile drops was measured using a GBX goniometer (Model Digidrop ++ GBX Scientific Instruments, Romans Sur Isère, France). Images were recorded using a CCD video camera. Uniform drops of liquid (3 μl) were carefully deposited on composite surfaces using Teflon syringes (5121 TLC-B Teflon, GBX Scientific Instruments) with an internal diameter of 0.73 mm. The analysed composite surface was brought to the drop with a motorised platform at room temperature ($23 \pm 3^{\circ}C$), and ambient humidity ($60 \pm 5\%$). Sample surfaces were previously washed with tap water, and finally dried for one hour at 40°C, thus allowing good reproducibility of the experiments (avoid handling contamination, dusts...). Before performing any measurement of a liquid droplet on a given surface, a kinetic study of the spreading was systematically carried out. This was done to prevent determination errors by ensuring that equilibrium was reached for each liquid used.



Probe liquids were chosen with medium or high surface tensions, in order to yield an accurate measurement and analysis of the experimental contact angle. Thus, five liquids were used as probes corresponding to pure water coming from reverse osmosis, glycerol, formamide, diiodomethane and ethylene glycol (Sigma-Aldrich, Lyon, France, analytical grade), respectively.

For each liquid used, contact angle measurement was done with 10 to 20 droplets as deposited on 20 mm × 50 mm surfaces. Both left and right contact angle were automatically calculated with the goniometer software. Due to roughness extent of the surfaces studied in the present work, surface free energy calculation could not be achieved directly. Indeed, we made the choice not to use Wenzel correction factors as this technique may in some cases be incorrect [11]. Consequently, the aim of this work is not to focus on the impact of surface roughening on surface free energy [12–13], but to discuss wetting behaviour to characterize surface preparation on the one hand, and to use contact angle as a tool to understand adhesion performance

on the other hand. No calculation was envisioned and contact angle measurement was utilized to compare surfaces with one another.

## 2.4. Roughness Measurements

Roughness was assessed by using laser interferometers WYCO NT 2000, VSI mode (VEECO Instruments, Dourdan, France). Ten roughness measurements were systematically made every centimetre, on $20\,mm \times 50\,mm$ composite surfaces. From all the available information, the $R_a$ parameter, representing the average roughness deduced from surface profile, was chosen for further discussion as being quite representative of the surface.

## 2.5. Optical Microscopy

Surface morphology assessment and fracture studies were done with a *LEICA DM LP* microscope (Leica, Rueil-Malmaison, France) which enables observations from $50\times$ to $500\times$ with polarized or non polarized light.



## 2.6. ToF-SIMS Analysis

Chemical analysis was performed with Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) apparatus: *TOF-SIMS IV (ION-TOF*, Munster, Germany). Analytical measurements were performed on an area of $50\,\mu m \times 50\,\mu m$, at a depth less than 10 Å (source: Au-25kV). Two areas were analysed for each sample. A semi-quantitative approach was made, taking into account a reference for both positive and negative ions.

## 2.7. Single Lap Shear Test

Destructive tests are the most investigated and used method to assess the surface adhesion ability. Hence, single lap shear tests were performed on $100\,mm \times 25\,mm$ specimens with a $12.5\,mm \times 25\,mm$ bonded area. Tensile lap shear strength of the adhesive (0.2 mm thick) (28.9 MPa at 25°C) was tested per ASTM D1002 after curing one hour at 177°C, on aluminium 2024-T3 treated with phosphoric acid anodizing according to ASTM D3933. Two samples with the same surface preparation were bonded together, then cured one hour at 180°C under 2.5 bars pressure. The final adhesive layer (epoxy film) has an approximate thickness of 0.2 mm. The epoxy formulation (Hysol EA 9689, Heakel, Baypoint, CA, USA) is a very wide spread one and

the filler contents (aluminium and silica) are nearly 40% weight. The supported film is also made with a glass weaving, this leading to a final density of 490 g/m$^2$. Glass/epoxy spacers were placed on one side of each bonded sample. Measurements were carried out at room temperature at 2 mm/min constant displacement rates on an *INSTRON 8802* (Instron, Canton, MA) apparatus with *Merlin*® software. The lapshear value was determined on five samples for each surface type, thus making it possible to calculate a representative average value and the typical error. For a similar surface preparation no significant variation of failure mode was observed for different specimens.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Surface Aspects

From the five treatments applied on metallic tools used for composite material preparation, one can consider only three different kinds of resulting surface morphology as visible on Figure 2 (similar aspects for both carbon/epoxy and glass/epoxy composites). Fluorinated film (A) (top) induces a very smooth and glossy surface clearly evidencing some protrusions of fibre reinforcement. The second type corresponds to the surface aspect created by the Frekoted tool (C and E) (middle) inducing some defects and scratches coming from the metallic tool preparation (grit or cutter) as visible on the second image. This surface aspect is completely similar for both Frekote preparation and dry ply preparation. Finally, the last surface aspect is obtained for both Teflon and Teflon + fluorinated film, these surfaces (B and D) (bottom) exhibiting a morphology corresponding to the imprint of the Teflon ply pattern. It is interesting to point out that, contrary to the Frekote and fluorinated film surface, Teflon roughness is only governed by the polymer thermoset resin. Indeed, the high roughness is due to the resin which is imprinted by the Teflon ply.

Average roughness values of both glass/epoxy and carbon/epoxy composite surfaces are reported in Tables 1 and 2, respectively. This roughness parameter is very similar when comparing surfaces prepared with Frekote or fluorinated film (A, C, and E from 0.4 to 1 μm). In addition, a roughness increase is observed for material prepared with Teflon ply (B and D) with a quite similar value (around 5.5 μm).

### 3.2. Surface Wettability

As surface roughness made it difficult to determine the surface free energy, contact angle values are compared from one surface to another

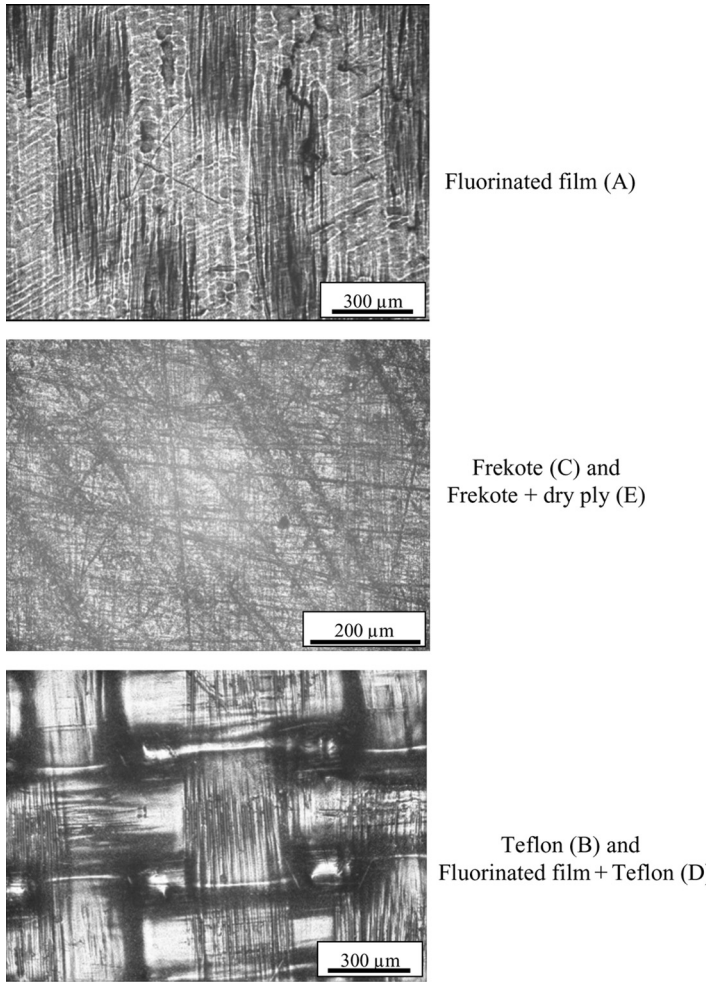


**FIGURE 2** Different surface aspects of glass/epoxy composites as evidenced by optical microscopy.

for the five liquids used. Results reported in Tables 1 and 2 indicate that for both material types the highest wettability is obtained for Teflon preparation (B). In this case, reported data clearly evidence that the extent of roughness induces increased wettability. On the contrary, surfaces obtained with fluorinated film + Téflon (D) have a similar roughness but significantly lower wettability values when compared with the Teflon treated one (B). This decrease may be mainly explained by chemical contamination resulting from the fluorinated film.

**TABLE 1** Contact Angle Assessment and Average Roughness for Glass/Epoxy Composite

| | Water | Glycerol | Formamide | Diiodo-methane | Ethylene glycol | $R_a$ (μm) |
|---|---|---|---|---|---|---|
| Fluorinated film (A) | 89.8 (±2.3) | 77.4 (±3.5) | 60.0 (±2.0) | 47.5 (±1.5) | 56.5 (±2.0) | 0.81 (±0.13) |
| Teflon (B) | 73.3 (±1.1) | 67.1 (±1.8) | 54.9 (±2.1) | 39.4 (±2.2) | 48.1 (±3.3) | 5.4 (±0.1) |
| Frekote (C) | 91.0 (±2.3) | 69.4 (±2.3) | 62.8 (±3.1) | 47.9 (±1.4) | 53.8 (±2.6) | 0.66 (±0.10) |
| Fluorinated film + Teflon (D) | 99.2 (±2.6) | 93.3 (±2.2) | 83.8 (±2.3) | 57.7 (±1.5) | 67.1 (±1.8) | 5.2 (±0.3) |
| Frekote + Dry ply (E) | 99.7 (±1.9) | 90.0 (±1.8) | 84.0 (±3.4) | 68.2 (±4.2) | 75.9 (±2.0) | 0.45 (±0.11) |

**TABLE 2** Contact Angle Assessment and Roughness for Carbon/Epoxy Composite

| | Water | Glycerol | Formamide | Diiodo- methane | Ethylene glycol | $R_a$ (μm) |
|---|---|---|---|---|---|---|
| Fluorinated film (A) | 90.4 (±2.8) | 75.7 (±1.6) | 64.7 (±2.7) | 43.4 (±3) | 58.9 (±1.9) | 0.8 (±0.2) |
| Teflon (B) | 77.8 (±2.0) | 68.5 (±3.2) | 55.0 (±2.7) | 36.7 (±1.5) | 47.9 (±2.2) | 6.9 (±1.2) |
| Frekote (C) | 68.0 (±8.0) | 65.7 (±1.6) | 49.0 (±1.3) | 38.4 (±4.0) | 51.1 (±1.0) | 0.97 (±0.2) |
| Fluorinated film + Teflon (D) | 95.9 (±2.1) | 86.4 (±1.4) | 80.3 (±2.8) | 55.9 (±1.4) | 65.9 (±2.0) | 5.4 (±0.9) |
| Frekote+ Dry ply (E) | 80.8 (±3.9) | 74.4 (±3.8) | 59.6 (±2.1) | 49.0 (±1.7) | 56.3 (±1.5) | 0.62 (±0.13) |

In addition, it is interesting to note that similar contact angle values are observed for both glass/epoxy and carbon/epoxy composite surfaces obtained from A, B, and D tool preparation. This experimental result shows that, in those cases, the surface chemistry and properties are not governed by the nature of fibre reinforcement but only by the composite resin, on the one hand, and the tool preparation itself, on the other hand [10].

The previous observation is not valid for a surface resulting from Frekote (C) preparation. In this case, the corresponding carbon/epoxy epoxy surface generally shows a much higher wettability when compared with the glass/epoxy one. Several concepts can be envisioned to explain such differences. The first explanation currently reported comes from the polar nature of glass fibre that will increase the polarity of the surface when it is protruding while carbon fibres do not [10,14–16], but it is actually fully controversial with results obtained here. The second reason that can explain the low wettability of glass/epoxy surface is that silicone compounds resulting from Frekote preparation may migrate onto the composite surface [17], preferably towards glass fibres when compared with carbon fibres as a consequence of the difference in chemical affinity. Such a surface contamination by the silicone derived compound may be responsible for a significant decrease of the glass/epoxy material's surface wettability. Such an explanation is consistent with the fact that in the case of a poorly wettable surface, any increase in roughness involves a decrease of the wettability, as already reported in the literature [18].

Finally, Frekote + dry ply preparation (E) shows a significant wettability gap when comparing carbon/epoxy with glass/epoxy composite surfaces. Again, this result may be explained by the silicone based contaminant migration from the Frekote. Such contamination is probably more important for this kind of preparation involving dry ply rather than for other Frekoted surfaces (C). Owing to fibre reinforcement which is directly in contact with a large Frekote area, glass fibre may contain more silicone based contaminant than a pre-impregnated ply. This result confirms, interestingly, the influence of fibre reinforcement on both the resulting surface contaminant and the migration of surface contaminant.



## 3. CHEMICAL ANALYSIS

A semi-quantitative approach to the different surface chemical compositions was envisioned using ToF-SIMS spectral analysis. Some of the data extracted from negative ions spectra, namely $^{19}F$ and $^{28}Si$, are reported in Table 3. Contrary to Teflon (B) and fluorinated film

**TABLE 3** ToF-SIMS (Negative Ions) Semi-Quantitative Results for Fluorine and Silicon

| | Carbon/epoxy fluorinated film A | Carbon/epoxy teflon B | Carbon/epoxy Frekote C | Glass/epoxy Frekote C |
|---|---|---|---|---|
| $^{19}F$ | 21103 (±2220) | 1600 (±125) | 465 (±125) | 451 (±170) |
| $^{28}Si$ | 2.5 (±0) | 7.1 (±0.7) | 483 (±195) | 817 (±40) |

preparation (A), it clearly appears that Frekoted surfaces (glass and carbon) exhibit no real fluorine contaminant coming from the surface preparation. Indeed, surfaces from preparation A show a significant surface contamination (with a high fluorine species content) probably caused by the migration or deterioration of the film release cloth during the manufacturing process. Although Teflon surfaces are made of fluorinated species, fluorine content appears one-tenth as high when compared with fluorinated film surfaces (respectively, 1600 and 21103, a.u.).

Such a surface chemical modification may explain poor surface wettability of fluorinated film treated samples. As an illustration, despite its higher roughness, surface samples as prepared with fluorinated film + Teflon (D) show significantly higher contact angles for the different liquids tested when compared with the Teflon (B) treated one. Moreover, the same surface shows a lower wettability when compared with the fluorinated film surface (A) which is smoother. This unexpected result indicates that the roughness increase aimed at enhancing the surface free energy remains an interesting procedure, as long as the initial untreated surface is already enough "wettable." Consequently, roughening a poorly wettable surface may actually reduce the surface wettability. Such a phenomenon was already pointed out by other authors [18].

Another main difference of surface chemical composition comes from the element Si, which is significantly higher in concentration on surfaces prepared by Frekote (C) (see Table 3). This point tends to confirm the transfer of the mould release agent from the metallic tool to the composite surface. In addition to that, this contamination by Si appears to be much more pronounced in the case of the glass/epoxy surface. Indeed, detected fragments containing Si atoms are characteristic of siliconed species. Considering the type of fragments analysed allows one to establish that the contaminant actually does not come from the silane coupling agent or from the degradation of glass fibre. As previously explained for wettability assessment, this

contamination gap may be due to the chemical nature of the reinforcing fibre that induces a higher chemical affinity for polar materials in the case of glass fibres when compared with carbon ones.

Finally, the whole interpretation allows to understand the low wettability of dry ply samples (E) directly stacked onto the Frekoted tool. Again, as the glass/epoxy surface naturally contains much more silicon species than the carbon surface, the present analytical approach allows confirmation that it induces a much lower surface wettability.

## 4. ADHESIVE TESTS

Single lap shear results and the fracture mode corresponding to the different surface preparations of resulting state of the surfaces are reported in Table 4. One can observe a good correlation between surface characterisation and lap shear values.

All assemblies prepared using fluorinated films (A and D) exhibit the lowest shear test performance with a fully adhesive fracture occurring at the adhesive-substratum interface. Both carbon/epoxy and glass/epoxy assemblies coming from D treatment show the lower lap shear value (140 daN). Despite a smaller roughness, specimens with only fluorinated film (A) show higher values when compared with the one prepared using D treatment. This last observation confirms that roughening poorly wettable surfaces actually does not induce significant adhesion enhancement. The difference observed between glass/epoxy and carbon/epoxy lap shear results (respectively, 306 and 495 daN) can not only be explained by the modulus material difference, but is also related to the fibre reinforcement protrusion as visible on Figure 2.



**TABLE 4** Single Lap Shear Tests and Fracture Mode

| | Lap shear results (daN) | | Fracture mode | |
|---|---|---|---|---|
| | Glass/epoxy | Carbon/epoxy | Glass/epoxy | Carbon/epoxy |
| Fluorinated film (A) | 306 (±45) | 495 (±66) | Adhesive | Adhesive |
| Teflon (B) | 586 (±23) | 591 (±46) | Mainly cohesive | Cohesive |
| Frekote (C) | 556 (±63) | 540 (±15) | Mix mode (cohesive and adhesive) | Mainly cohesive |
| Fluorinated film + Teflon (D) | 134 (±21) | 146 (±29) | Adhesive | Adhesive |
| Frekote + Dry ply (E) | 326 (±13) | 597 (±5) | Mainly adhesive | Mainly cohesive |

Assemblies resulting from Teflon (B) and Frekote (C) surfaces present the highest lap shear results with a predominantly cohesive rupture inside the composite material at the fibre-resin interface. Owing to its roughness and low contaminant content, Teflon treated surfaces (B) appear more cohesive than Frekote treated ones. It is quite important to note that despite a much higher Si contamination related to Frekote use, glass/epoxy surfaces reach lap shear values equivalent to those of carbon/epoxy material. It is then surprising to observe that in this last case migration of the mould release agent onto the composite surface does not induce any loss of mechanical performance.

Finally, assemblies corresponding to surfaces prepared with Frekote + dry ply (E) tool preparation show a different behaviour when comparing carbon/epoxy with glass/epoxy. Firstly, lap shear values appear significantly higher for carbon/epoxy assemblies. In terms of wettability, these results are in agreement with theoretical considerations since the glass/epoxy composite surface is less wettable than the carbon/epoxy one. This result is also in good accordance with ToF-SIMS analysis, thus indicating that migration of mould release agent is more pronounced in the case of the glass/epoxy composite surface than for carbon/epoxy. As already mentioned above, lap shear performance is, therefore, significantly lower for glass/epoxy with a predominant adhesive fracture.



## 5. CONCLUSIONS

The present study clearly illustrates that topographical, chemical, and wettability studies enabled us to understand better the composite surface behaviour resulting from a given tool preparation. Correlations between surface characteristics and single lap shear results have also been established.

Among all the surface preparations tested, the Teflon one gives the highest lap shear results; indeed, this ply induces only a slight fluorinated contamination but a highly wettable substrate with suitable roughness. In this case, correlation between surface properties and lap shear results has been evidenced with a fully cohesive fracture when Teflon is used. Furthermore, the extent of surface roughness limits the fibre reinforcement's influence as the corresponding surface properties are, therefore, mainly influenced by the polymer matrix.

In addition to that, fluorinated contamination and migration of mould release agent related to the tool preparation step have been clearly shown, and their effects on the assembly properties were established. It is obvious that reinforcing fibres actually play a determining

role not only on surface ability to adhere but also on the contamination resulting from the tool preparation mode.

The different experiments also enabled the demonstration that surface roughening of initially poorly wettable samples is not an accurate method to increase wettability properties as adhesion ability remains inadequate.

As widely known, surface preparation prior to bonding needs very specific care; the present work underlines that independently to any additional surface treatment (like grit blasting, mechanical abrasion, etc.), mould surface preparation is of primary importance as it may induce important composite surface modifications that have a considerable effect on further properties such as bonding ability and performance.

## ACKNOWLEDGMENTS

This work was supported by Aircelle Le Havre (SAFRAN Group, France), region Haute-Normandie (France) and the Fond Européen de Développement Régional (FEDER). The authors are grateful to Aircelle Le Havre for supplying samples and particularly to Dr. Frederic Joubert for helpful discussions. Further thanks go to Pr. Jean Louis Izbicki and Dr. Bruno Morvan of L.A.U.E (Le Havre University, France) for the use of the laser interferometer. Finally we appreciated the help of members of Plate Forme Technologique (Le Havre University) for the use of the mechanical testing machine. The authors dedicate the present article to the memory of deceased Prof. TK Wang.



## REFERENCES

[1] Raper, K. S., Roux, J. A., McCarty, T. A., and Vaughan, J. G., *Composites: Part A* **30**, 1123–1132 (1999).
[2] Gadam, S. U. K., Roux, J. A., McCarty, T. A., and Vaughan, J. G., *Composites Science and Technology* **60**, 945–958 (2000).
[3] Fernlund, G., Rahman, N., Courdji, R., Bresslauer, M., Poursartip, A., Willden, K., and Nelson, K., *Composites: Part A* **33**, 341–351 (2002).
[4] Twigg, G., Poursartip, A., and Fernlund, G., *Composites: Part A* **35**, 121–133 (2004).
[5] Fung, C. P., *Wear* **254**, 298–306 (2003).
[6] Allen, K. W., *Int. J. Adhesion and Adhesives* **13**(2), 67–72 (1993).
[7] Roizard, X., Wery, M., and Kirmann, J., *Composite Structures* **56**(3), 223–228 (2002).
[8] Kim, J. K. and Lee, D. G., *Composite Structures* **57**, 37–46 (2002).
[9] Crichtlow, G. W., Cottam, C. A., Brewis, D. M., and Emmony, D. C., *Int. J. Adhesion and Adhesives* **17**, 143–150 (1997).
[10] Bénard, Q., Fois, M., Grisel, M., Marchant P., and Perrot, C., "Journées de l'Adhesion," Conference, Oléron (France), 1–3 Oct. 2002, pp. 161–164.

[11] Wolansky, G. and Marmur, A., *Colloids and Surfaces* **156**, 381–388 (1999).
[12] Della Volpe, C., Penati, A., Peruzzi, R., Siboni, S., Toniolo, L., and Colombo, C., *J. Adhesion Sci. Technol*. **14-2**, 273–299 (2000).
[13] Nakae, H., Inui, R., Hirata, Y., and Saito, H., *Acta Mater*. **46**(7), 2313–2318 (1998).
[14] Bénard, Q., Fois, M., and Grisel, M., *Applied Surface Science* **253**, 4753–4758 (2007).
[15] Bénard, Q., Fois, M., and Grisel, M., *Int. J. Adhesion and Adhesives* **25**, 404–409 (2005).
[16] Dilsiz, N. and Wightman, J. P., *Carbon* **37**, 1105–1114 (1999).
[17] Vickers, P. E., Boniface, L., Pricket, A., and Watts, J. F., *Composites: Part A* **31**, 559–569 (2000).
[18] Busscher, H. J., Van Pelt, A. W. J., De Boer, P., De Jong, H. P., and Arends, J., *Colloids and Surfaces* **9**, 319–331 (1984).