JOURNAL OF MATERIALS SCIENCE **34** (1999) 4203–4208

# Morphology of the outermost layer of a compression molded composite based on unsaturated polyester resin

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Composites materials, SMC and BMC are widely used for the manufacture of automotive parts. These high performance materials are characterized by their superior surface quality. A strict control of the surface quality goes through a good knowledge of the surface and of the outermost layer. The present work is dedicated to composites surfaces knowledge. The studied material was a compression mold thermosetting composite based on unsaturated polyester resin. Different components like mold release agent, mineral fillers as calcium carbonate and glass fibers were introduced in the resin to prepare the composite. With SEM, XPS and AFM which are techniques dedicated to characterize the surface and the outermost layer, we were able to identify and locate each component in the outermost layer. The mold release agent was found at the surface. The other components were deeper localized. Although they are more than 0.4 $\mu$m deep, the glass fibers have an impact on the topography of the surface. A surface layer model was proposed. © *1999 Kluwer Academic Publishers*

## 1. Introduction

Composites materials, Sheet Molding Compound (SMC), Bulk Molding Compound (BMC) are extensively used in the automotive industry. These thermosetting compounds contain an unsaturated polyester resin, mixture of an unsaturated polyester polymer (40 wt %) with a vinyl monomer (60 wt %), usually styrene. The polymer is obtained from an esterification of diacids (or acid anhydrides) with diols and a polycondensation. One example of unsaturated polyester is a mixture of maleic anhydride with phthalic acid and glycol. In order to reduce the shrinkage, low profile additive is introduced (8–16 wt %) in the mixture [1, 2]. The phase separation between the polyester resin and the additive plays an important role in the formation of microstructures [3, 4]. The additive also enhances product surface finish [5]. Inorganic fillers are also introduced in thermosetting resin in order to adjust the rheological properties for the optimisation of the transport of the reinforcement components, to reduce the amount of resin used and to minimize the cost of production. Calcium carbonate is widely used for these purposes. Several authors including Kubota [6] and Lem and Han [7] have demonstrated that fillers increase the viscosity of the polyester resin [6, 7]. Glass fibers to reinforce the composite (15–20 wt %) are used to improve the mechanical properties. Other components, such as mold release agents, polymerization initiators are also present at less than 2 wt %.

For some applications, a good surface finish has to be obtained. For such goal, the composition of the composite, plays a key role. For example, the filler percentage and the fiber volume influence the gloss and the roughness of the surface [8]. Parameters of the molding process, such as molding pressure, molding temperature are also determinants for a good surface finish [9]. Although some parameters have been shown to influence surface finish [8, 9], no explanation was given. To achieve this, a better knowledge of the surface and of the outermost layer is necessary. That is the purpose of this work.

We examined a thermosetting composite molded by compression. Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) were used to characterize the surface and the outermost layer.

## 2. Experimental

The studied material was based of an unsaturated polyester resin (18 wt %). The composite material was also composed by (i) mineral fillers (73 wt %) within 67% of calcium carbonate (particles in range 1–10 $\mu$m with a mean of 3 $\mu$m), (ii) low profile additive (8 wt %), (iii) internal mold release agent (calcium stearate) (1 wt %) (particles in range 2–13 $\mu$m), (iv) glass fibers (20 wt %). The glass fibers were 12 $\mu$m wide and were of two types: short fibers, which are 100 $\mu$m long and long fibers, which are between 4 and 6 mm long. Plates ($190 \times 210 \times 3\ \mathrm{mm}^3$) were manufactured using a Derek press in a mould with a very high level of polishing. The polished female part is heated at 150 °C and the punching die at 135 °C. The pressure applied on the composite is 100 bars. The curing time is 100 s. Samples ($10 \times 10\ \mathrm{mm}^2$) were taken from the plaques at different places and examined by SEM, XPS, and AFM. Samples from seven identified places were examined and the results were compared. We arrive to the conclusion that as far as SEM, EDX, XPS and qualitative AFM are concerned, the plates were homogeneous.

Scanning Electron Microscopy (SEM) provides the morphology of the outermost layer of the surface. Energy Dispersive X-ray Spectrometry (EDX) gives the composition of the components constituting this layer. SEM and EDX were carried out on a HITACHI S 4200 combined with an OXFORD Analyzer controlled by LINK ISIS software. In order to be examined, the samples were carbon-coated. The penetration depth of the electrons in a material is a function of the operating voltage, the density of the material, of its atomic number, according the given semi-empirical law [10].

The SEM was operated at different operating voltages (1, 5, 10, and 15 kV). As shown in Table I, the electron penetration depth depends on the operating voltage. SEM images are composed by secondary electrons emerging from about at most 20 nm deep and by backscattered electrons for which the production depth depends on the energy of the incident electron beam and allows different depth imaging from the surface (Table I) [11]. As the operating voltage is enhanced, the backscattered electrons become predominant.

X-ray Photoelectron Spectroscopy (XPS) is a well-established tool for surface analysis. The data obtained by this technique provide information about the chemical constitution and bonding of the surface elements. Generally, only photoelectrons generated within the outermost 10 nm surface layer are detected.

XPS measurements were carried out on a VG ESCALAB MKII equipped with 200 W Al$K_\alpha$ and Mg$K_\alpha$ sources, a multidetection analyzer controlled by VG eclipse software. As the samples are isolating, we fixed the binding energy of the main peak of the carbon C1s at 285.0 eV, typical binding energy of the aliphatic carbon.

TABLE I Variation of the electron penetration depth with SEM operating voltage. These evaluations were performed using the semi-empirid law [10] using a material of density 1.75

| SEM operating voltage (kV) | Incident electron penetration depth ($\mu$m) | Information depth ($\mu$m) as proposed in Ref. [10] |
|---|---|---|
| 1 | 0.7 | 0.02 |
| 5 | 0.9 | 0.15 |
| 10 | 1.5 | 0.4 |
| 15 | 3 | >1 |

Atomic Force Microscopy (AFM) gives the topography 3D of a surface at the nanometer scale and allows determination of the roughness of the surface. AFM measurements were carried out on a Pico SPM manufactured by Molecular Imaging operating with a Nanoscope E controller from Digital Instrument Corporation. The scanner was able to sample a horizontal scanning range of 23 $\mu$m and a vertical scanning range of 7 $\mu$m. Microfabricated $Si_3N_4$ gold coated cantilevers, 250 $\mu$m length, with integrated $Si_3N_4$ pyramidal tips were used. The spring constant of the cantilevers was 0.06 N/m. During the surface scan, the tip was always in contact with the surface.

Unless specified otherwise, all the analyses (SEM, EDX, XPS, AFM) were performed on the side of the sample in contact with the polished female part of the mould. The observed composite was named A, it was filled with calcium carbonate, the mold release agent was calcium stearate.

## 3. Results and discussion

On the SEM imaging, we first examined the influence of the operating voltage in such a way to examine the composite morphology more and less deep. The entire sample surface was explored. Fig. 1 shows representative SEM images of composite type A (fiber length 100 $\mu$m) of this statistical examination. The images in Fig. 1 were taken at the same place at 1, 5, 10, 15 kV. At 1 kV, a granular surface was noted. Fig. 1b showed fibrous structure and the presence of a fiber was suggested. At 10 kV mineral fillers and a fiber were observed. The shapes of the components became more and more distinctly visible at 15 kV. The mineral fillers were distributed non homogeneously and surrounded the fibers, which laid parallel to the surface. At 10 kV, EDX analysis allow to identify the fibers and calcium carbonate fillers, where respectively silicon and calcium were detected. All these results indicated that there was a heterogeneous distribution of the different components. The calcium carbonate fillers were under the surface and the fibers located deeper than 0.4 $\mu$m.

We also examined by SEM a slice of a plate type A (fiber length 100 $\mu$m) broken by Charpy impact perpendicularly to the surface of the plate. We have to distinguish the two sides of the plate: the side in contact with female part of the mould heated at 150 °C and the side in contact with the punching die heated at 135 °C. Fig. 2a and b showed respectively two places of the slice of a sample, at the outer surface where the compression was applied and near the under surface. On Fig. 2 no special morphology were seen apart from small disks 12 $\mu$m in diameter which were in fact the section of the fibers. These disks seem to be empty or full depending where the fibers were broken. No fiber was detected on the surface and this fact confirmed the observation of the Fig. 1. The comparison of the two images showed that the glass fibers were more numerous in Fig. 2b than in Fig. 2a. The fibers were more scattered in the outermost layer where the pressure was applied.

We studied the influence of the glass fiber length on a composite type A (Fig. 3). One plaque type A was

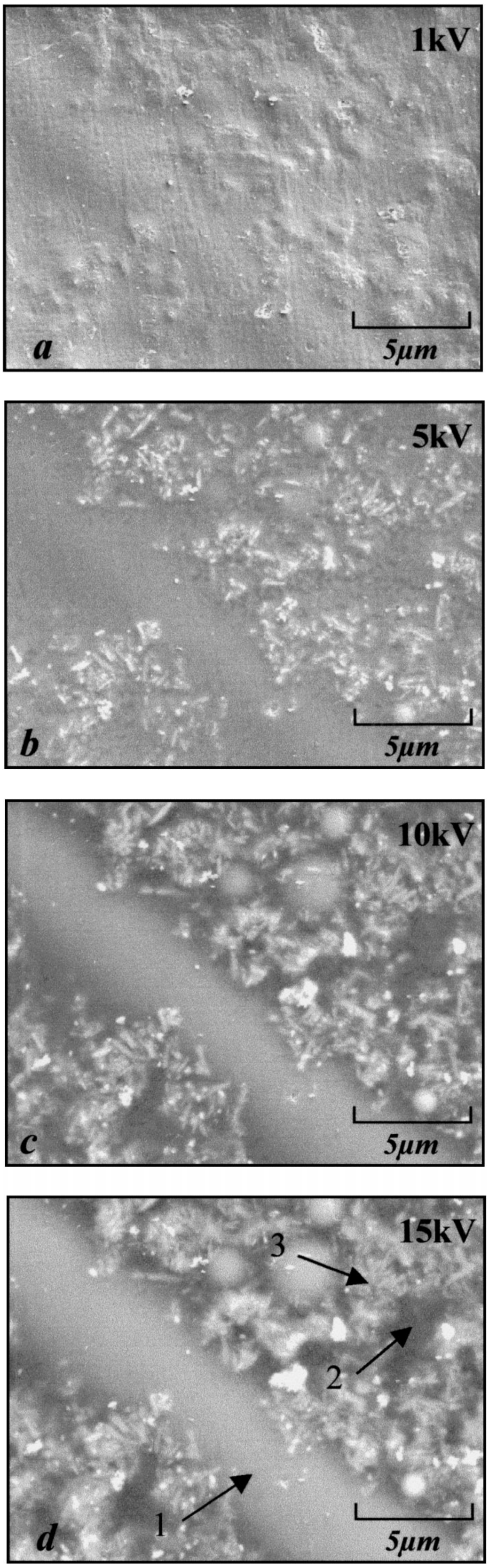


*Figure 1* SEM images of thermoset polymer composite type A (fiber length 100 $\mu$m) sample taken at operating voltage of (a) 1 (b) 5 (c) 10 and (d) 15 kV. The arrows 1, 2, 3 indicate respectively (1) fiber, (2) resin and (3) calcium carbonate filler.

TABLE II Characteristics of the composites ABC

| Name of the composite | Release agent[a] | % m[b] | Fillers[a] | % m[b] |
|---|---|---|---|---|
| A | Calcium stearate | 0.1 | $CaCO_3$ | 17 |
| B | Calcium stearate | 0.1 | $Al(OH)_3$ | 16 |
| C | Aluminum stearate | 0.06 | $Al(OH)_3$ | 17 |

[a] Nature of the mold release agent and of the mineral filler.

[b] Percentage in weight of calcium and aluminum in the composite due to the release agent or due to the fillers.

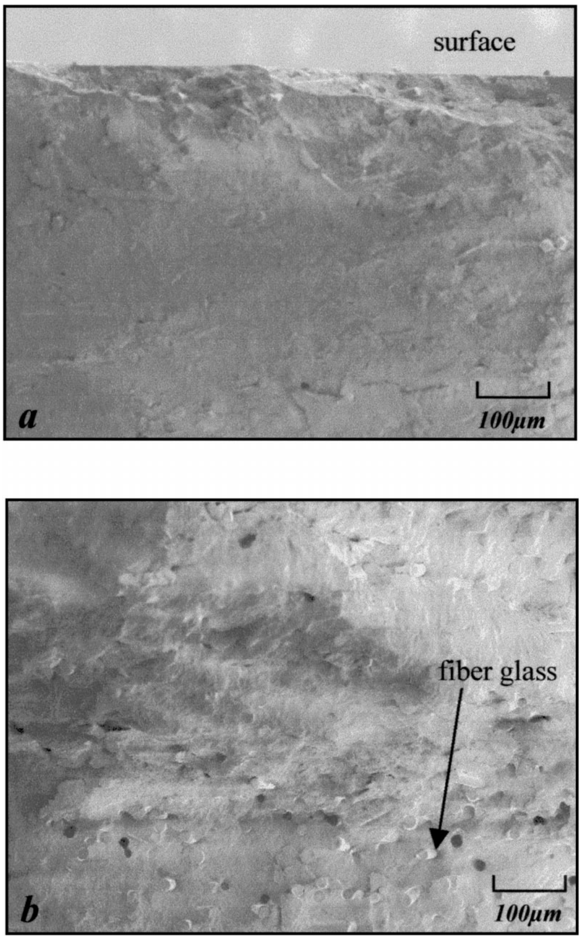


*Figure 2* SEM images (operating voltage 10 kV) of a slice of a plaque cut perpendicularly to the surface. The composite was of type A with fiber 100 $\mu$m long: (a) Near the surface where the compression was applied; (b) on the other face of the plaque.

manufactured with short fibers (100 $\mu$m) and an other was manufactured with long fibers (4–6 mm). Samples were examined by SEM. Fig. 3a and b show images at an operating voltage of 10 kV, we supposed that the same depth was investigated in these samples. It is necessary to remember that the short fibers and the long fibers have the same diameter (12 $\mu$m). However, on the SEM images, the long fibers appeared bigger than the short fibers. This means that the long fibers were closer to the surface than the short fibers. The length of the fiber had an influence on its position towards the surface.

Some BMC were prepared by modifying the nature of the mineral fillers and of the release agents as reported in Table II. The samples were characterized in XPS for which the analysis depth is 10 nm. The XPS spectrum (Fig. 4(1)) reported the presence of carbon (79–80 at%) and oxygen (20–21 at%) as main elements, with a little amount of calcium (Fig. 4 and Table III).

The C1s and the O1s spectra are shown in Fig. 4(2). In the literature [8], the C1s peaks of organic polymers have energies ranging from 284.7 eV for aromatic CH to 290.4 eV for OCOO carbon. In the present work, the C1s spectrum was composed of a main peak at 285 eV and two small peaks at 286.5 and 289.2 eV. The C1s spectrum of our sample could be attributed to organic carbon with contributions of aromatic carbon, aliphatic carbon at 285 eV and COR carbon at 286.5 eV and also COO carbon at 289.2 eV.

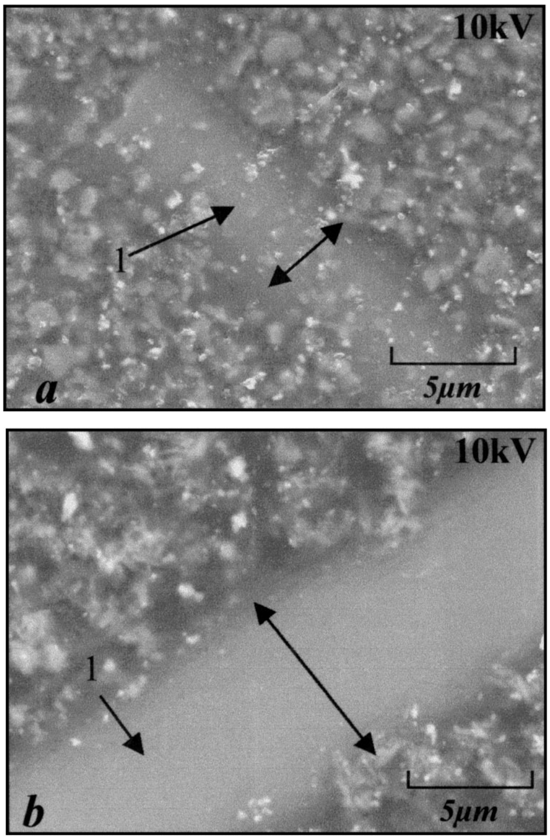


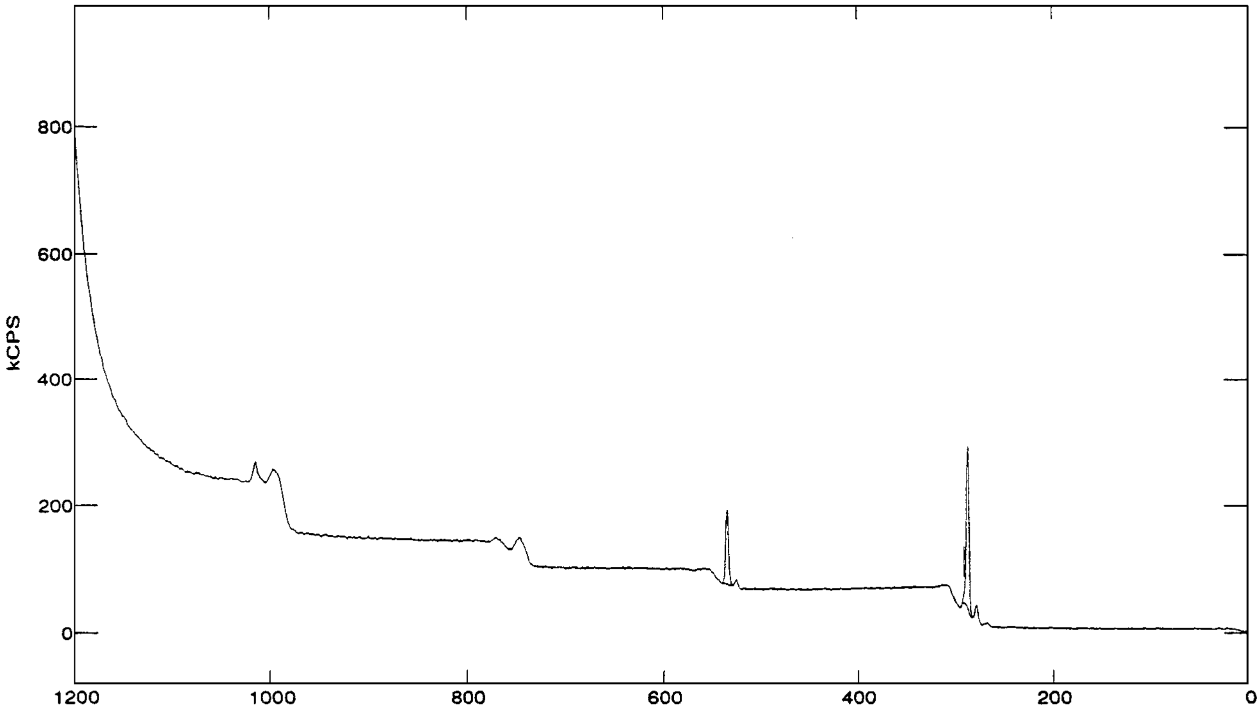
*Figure 3* SEM images (operating voltage 10 kV) of thermoset polyester composite samples type A. The arrow 1 indicate the location of the fibers: (a) The fibers are 100 μm long; (b) the fibers are 4.5 mm long.

TABLE III Mass percentage of the elements carbon, oxygen, calcium and aluminum as detected by XPS for three composite A, B, C defined in Table II. In column Ca 2p 3/2 and Al 2p 3/2 are given the mass percentage of the element as seen in XPS

| Name of the sample | C | O | Ca | Al |
|---|---|---|---|---|
| A | 78 | 21 | 0.6 | — |
| B | 79 | 20 | 0.6 | No detected |
| C | 79 | 20 | — | 0.85 |

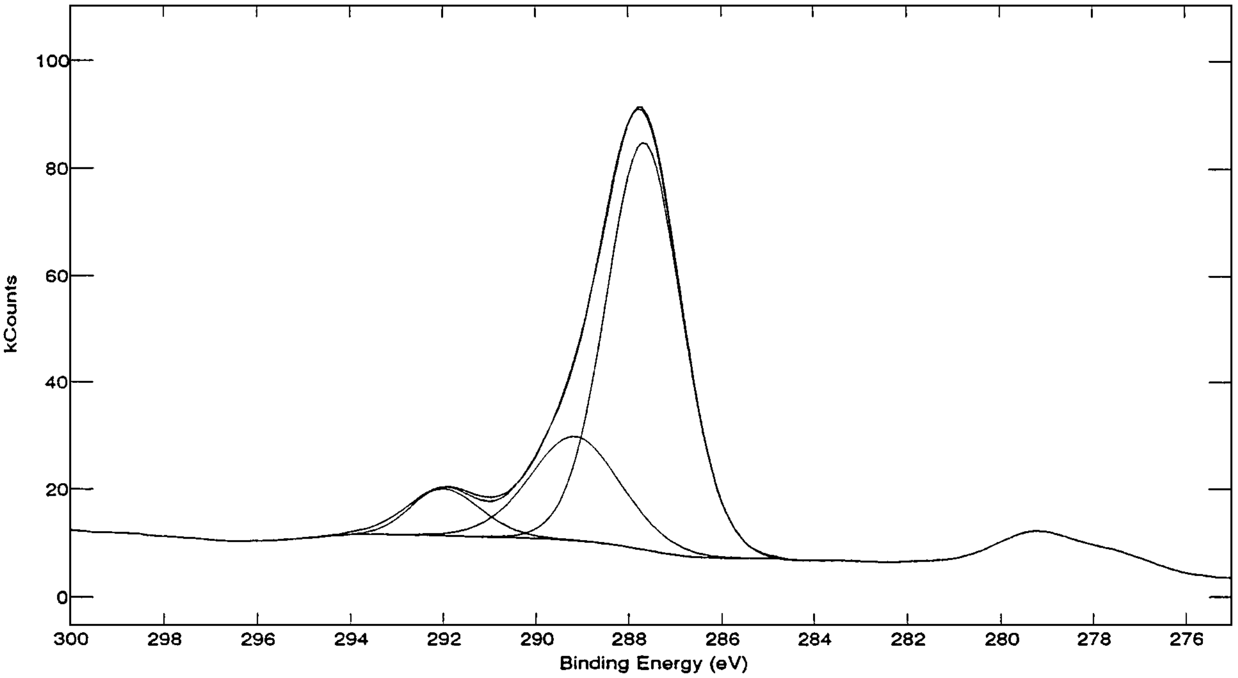
The O1s peak energies of polymers are ranging from 531.6 to 533.9 eV [12]. The observed O1s spectrum was composed of a broad peak at 533.8 eV and could come from oxygen in organic polymer.

Traces of calcium were also detected. The calcium could derive from the internal release agent (calcium stearate) or from the fillers (calcium carbonate). To determine the origin of calcium present at the surface, we examined by XPS samples with different fillers and release agents as presented in Table II. The presence of calcium and aluminum in XPS spectra was returned in Table III. When calcium stearate was used as release agent even with calcium free fillers, calcium was detected (sample B). When aluminum was used as filler with calcium as mold release agent (sample B), aluminum was not detected by XPS. Aluminum was detected only when it was used as release agent (sample C). From the comparison of the three composite samples (A, B, C), we concluded that only the mold release agent was detected in XPS and that within the first 10 nm from the surface, only the mold release agent was

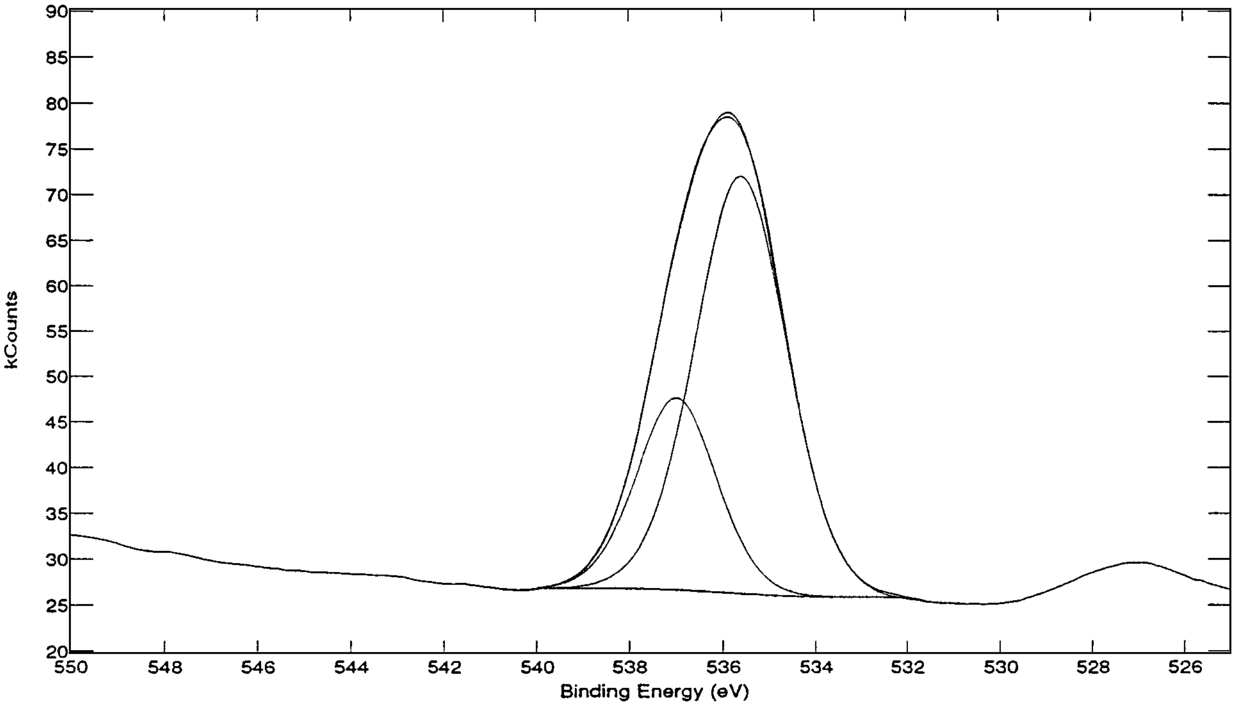


(1)

*Figure 4* XPS spectrum of the thermoset polyester composite type A sample: (1) Wide scan XPS spectrum (2a) C1s spectrum (2b) O1s spectrum. (*Continued*).



(2a)



(2b)

*Figure 4* (*Continued*).

present, the fillers were located deeper. To complete our investigation, we noted that no silicon was detected, indication of the absence of glass fiber within the first 10 nm from the surface.

We concluded from all these XPS results that the mold release agent is present at the surface and that the outermost layer explored by XPS, 10 nm deep has an organic composition.

Fig. 5 shows representative AFM images of the surface of a composite type A sample (fiber length 100 $\mu$m). Fig. 5a showed only polishing marks coming from the mold steel plates. The Arithmetical Mean Deviation roughness was 10 nm. In Fig. 5b, we saw a *fiber-like feature* which was 2 $\mu$m wide and 150 nm high. From XPS and SEM we knew that the fibers were localized in depth. The modification of the topography of the surface was due to a fiber, localized in the volume, 1 $\mu$m under the surface. This important observation means that even if the fiber was 1 $\mu$m deep, it had an impact on the topography of the surface. Thus, the roughness of the surface was more important (14 nm).

All these previous results lead to a model of the outermost layer of an unsaturated polyester composite material molded by compression as shown in Fig. 6. XPS showed the existence of an organic layer, which is at least 10 nm thick, with the mold release agent within

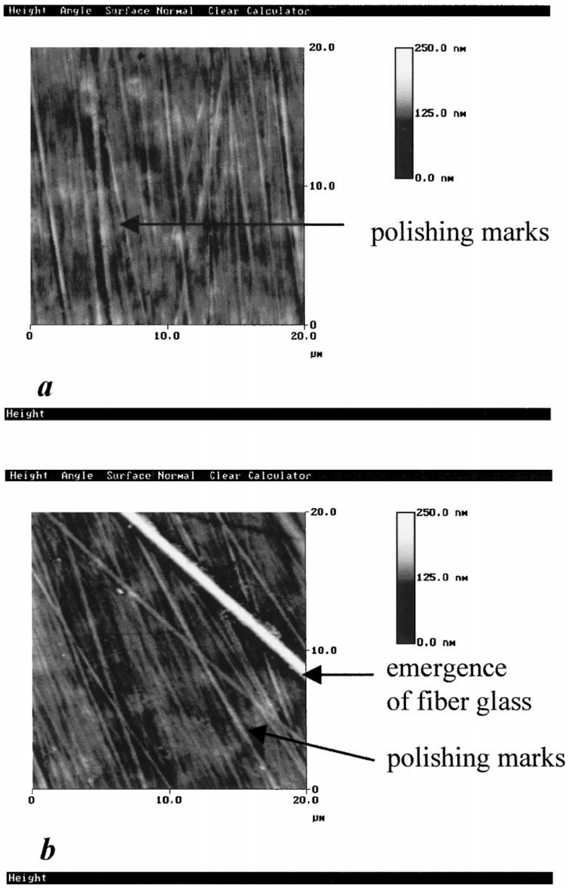


*Figure 5* AFM images of the surface of the thermoset polyester composite type A (fibers 100 $\mu$m long) sample: (a) Typical image when no emergence of a fiber are detected; (b) typical image when the emergence of a fiber is visible.

this layer. The fibers and calcium carbonate fillers were outer this organic layer. We showed that the first fibers were located, more than 0.4 $\mu$m deep and were parallel to the surface. As shown by AFM these fibers had an impact on the topography of the surface.

## 4. Conclusion

This work showed that combined techniques allow to achieve pertinent information on the distribution of the components of an unsaturated polyester thermoset composite. Position of the fibers, the release agents, the calcium carbonate fillers were explored. Thanks to a SEM analysis at different operating voltage combined with EDX, the location of these components toward the surface was determined. XPS give the composition of the 10 first nm of the volume and the AFM analyzes the topography of the surface. These results give a better knowledge of the outermost layer of the composite and allow the proposition of a model. This present methodology of characterization can be applied with all composite materials. Morphology modifications due to composition modifications or process modifications could be explored. This information could have a great interest in industry.

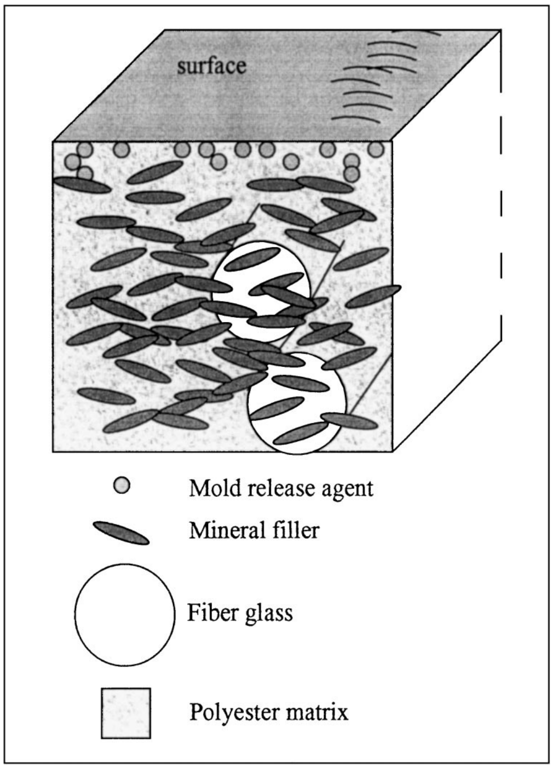


*Figure 6* Model of the outermost layer of a polyester composite material molded by compression with (1) large circles: fibers, (2) medium circles: calcium carbonate fillers, (3) small circles: mold release agents.

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*Received 30 July*
*and accepted 11 December 1998*