SHAPE MEMORY COMPOSITE SANDWICH WITH SELF-HEALING PROPERTIES FOR MARINE APPLICATIONS

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ABSTRACT

In this study, the feasibility of the production of a shape memory composite (SMC) sandwich with self-healing properties is discussed. Prototypes have been made by using thin carbon fibre laminates for skins and SMP foams for core. Two different foams have been used: thermoplastic (PET) and thermosetting (epoxy). Small sandwich samples have been tested in bending up to failure and subsequently recovered by using a hot air gun. Such samples were recovered after coating the failure zone with a small amount of uncured epoxy resin, in liquid state. That was a method to simulate the self-healing function. Subsequently, bending tests have been repeated to evaluate residual properties of composite sandwiches.

1 INTRODUCTION

Shape memory polymers (SMPs) are a very attractive class of materials because of their stimuli-responsive nature. In fact, SMPs have the capability of changing their shape upon application of an external stimulus. The stimulus is mostly heat, but light, electric and magnetic fields may also be used. For the heat-activated SMPs, the shape memory effect can be observed by performing a typical thermo-mechanical cycle. Firstly, the polymer is processed to receive its permanent shape. Secondly, it is heated and deformed in a new configuration that can be stored by cooling. Heating up the SMP above a transition temperature (which is the glass transition temperature, Tg, for the thermoset polymers) it recovers its original shape. [1]

Shape memory composites (SMCs) can be produced by using SMPs. If fibres or particles are added to the SMP, shape memory properties can be reduced with the advantage of increasing strength and dimensional tolerance [2]. SMCs combine typical mechanical and functional properties of composites with shape memory properties of SMPs. In a polymeric matrix composite (PMC), shape memory properties are typically given to the resin matrix as fibres do not show any important material transition. However, other technical solutions are possible and, in such cases, preferable: applying flexible composite skins over a shape memory foam core seems to be very promising for producing composite sandwiches [3]. In marine applications, SMCs could be used to develop new foldable small boats: for example sea kayaks are popular sports gear, but storage space for them is limited in such countries like Japan [4].

Apart from volume reduction, another interesting application in marine field is self-repairing of boats or marine structures after impact. Self-healing is the ability of the composite to fix the damage occurred after impact, mainly in the case of matrix failure [5]. Self-healing reflexive composite structures, originally developed for application in unmanned aerial vehicles, have been adapted to function in a marine environment [6]. Reflexive structures combine healable resin, structural health monitoring, and integrated autonomous repair for increased survivability in composite vehicles and structures. Adapting this proven reflexive solution to marine environments involved the development of a marine-compatible resin and the optimization of signal parameters for SHM functionality underwater.

In previous studies, it has been shown that SMCs have good self-repairing properties at least in terms of shape recovery [7]. A further development is integrating the additional self-healing function. This function can be obtained, for example, by mixing small hollow microspheres in the foam core:
these spheres can be filled with a resin precursor and a catalyser. In the case of an impact, the SMC structure could be dramatically deformed with cracks and delamination: this energy would also break the microspheres, making contact between uncured resin and catalyser. If the SMC structure is locally heated, e.g. by means of a hot air gun, the shape is recovered due to the SMP and cracks are partially closed due to the resin polymerization.

In the current study, the self-healing function has been prototyped by coating the crack surface with a small amount of uncured epoxy resin. During heating, SMC sandwiches recovered the initial shape and contemporarily resin polymerization was achieved.

2 MATERIALS AND METHODS

Several composite sandwiches were produced for the study, for all of them carbon fibre (CF) composite skins were used together with a SMP foam core. Two foams were selected: a commercial PET foam and an epoxy foam by solid state foaming. In one case, a SMP interlayer was also added between the CF plies of the composite skins. Bending tests were used to evaluate initial and residual stiffness and strength of sandwiches before and after damage recovery.

2.1 Raw materials

Commercial materials were used for the experimentation. SMP interlayer and epoxy core foams were produced by using an epoxy resin (3M Scotchkote 206 N) which was available as an uncured green powder, and was a one-part, heat curable, thermosetting epoxy coating. Composite skins were made with CF reinforced prepgres (HexPly by Hexcel) with a 42 wt% epoxy resin content and a nominal area weight of 345 g/m². This kind of prepreg is a 0/90 fabric typically used for aeronautical applications: its epoxy matrix shows high stiffness and strength without any shape memory behaviour.

The PET core foam was made of virgin PET and was used as received with a thickness of 15 mm and a density about 70 kg/m³. Composite skins were attached to the PET core foam by gluing with an epoxy adhesive (Pattex Power Epoxy). In the case of epoxy foam cores, the same powder used for foaming was also used for adhesive joining.

In order to simulate the self-healing function, a commercial epoxy resin (Duraloid AL-30 by Prochima) was used to cover the cracks. Resin polymerisation was achieved by using a hot-air gun simultaneously with shape recovery of composite sandwiches.

![Tablet positioning for the production of epoxy core foams.](image)

2.2 Foaming of epoxy cores

In previous studies, a new foaming technology (solid state foaming) was developed which is able to produce thermosetting foams by directly over-heating solid tablets of uncured resin [8, 9]. Such foams exhibit good shape memory properties and are interesting for space applications [10]. Composite foams can be obtained by mixing uncured resin powders and fillers, and pressing the mixture to make the tablets. MMT filled SMP epoxy foams have been studied and good results were obtained in terms of shape memory properties and structural properties [11].

In the current study, epoxy foams were produced by solid state foaming. Starting from the thermosetting powder, tablets were shaped by means of cold compaction in a cylindrical stainless steel mould. The internal diameter of the mould was 20 mm and final tablets had a height of 10 mm and a weight about 4 g. The cold compaction was performed by means of a universal testing machine (MTS Alliance RT50) to carefully control the process parameters (maximum packing pressure of 130 MPa, packing rate of 10 mm/min, holding time of 1 min). The epoxy powder was used ‘as received’ and no
blowing agent was mixed together. Next step was foaming the tablets by means of the insertion in a muffle at 320°C for 8 min. The foaming process was performed in air, placing the tablets in cylindrical metallic container: 5 tablets at a time were used to have long samples (Figure 1).

After foaming, the mould was left to cool in air, and the samples were extracted from the moulds. As a last operation, the samples were machined for sizing, eliminating the external surfaces. Final size of the epoxy foams was about 90x15x13 mm³ with a density about 380 kg/m³.

### 2.3 Molding composite skins

Two-ply composite skins were produced by moulding with a hot parallel plate press at low pressure (1.5 bar), a plate temperature of 150 °C and a moulding time of 20 min. A thermoplastic film was used as mould release. Two different sizes were selected for the composite skins in the case of PET foam core (120x30 mm²) and epoxy foam core (90x15 mm²). In both cases, the laminate thickness was about 0.4 mm. Shape memory composite skins were also produced by placing a 150 µm SMP interlayer between the two plies. During lamination, the SMP resin was placed on the first prepreg layer in the shape of uncured resin, subsequently the second prepreg layer was placed on the first one. SMC skins were used only with the epoxy foam core.

![Figure 2: SMC sandwiches with PET (left) and epoxy (right) foam core.](image1)

### 2.4 Sandwich production

Composite sandwiches with PET foam core were produced by gluing the skins over the foam. A pressure of 0.2 bar was applied for 6 h for a better adhesion. Final size of CF/PET sandwiches was 120x30 mm² with a thickness about 16 mm.

In the case of epoxy cores, skin-core joining was achieved by means of the same resin powder which was already used for SM cores and interlayers. The adhesion was achieved after placing the resin powder at the interfaces and curing at 150°C for 5 min at low pressure (0.5 bar). The final thickness of the adhesive interface was estimated to be about 100 µm. Final size of CF/Epoxy sandwiches was 90x15 mm² with a thickness about 14 mm. Figure 2 shows two sandwich samples: the first having a PET foam core, and the second with an epoxy foam core.

![Figure 3: Bending tests on SMC sandwiches with PET (left) and epoxy (right) foam core.](image2)
2.5 Testing

Three point bending tests were used to mechanically qualify SMC sandwiches (Figure 3). Tests were performed up to failure at the rate of 10 mm/min and a span of 100 mm for CF/PET sandwiches, 70 mm for CF/Epoxy sandwiches. Failure was directly detected by the testing machine (MTS Insight 5). After failure, shape recovery of sandwiches was achieved by heating with a hot-air gun. Before shape recovery, a liquid uncured epoxy resin was distributed in the crack regions of such samples so as to simulate the self-healing function. After shape recovery, sandwiches were tested again under bending to evaluate the residual properties.

3 RESULTS

Several failure mechanisms were observed during bending also in dependence of the foam typology. In CF/PET sandwiches, cracks were localized on the CF skin in contact with the push rod (Figure 3) whereas the PET foam under the cracks tends to collapse. In CF/Epoxy sandwiches, foam collapse was present only at low displacements. By increasing the displacement, large cracks occurred also in the epoxy foam as well as failure of the skin-core adhesive interface. Figure 4 highlights this difference which is probably dependent on the different density of the foam cores.

Figure 5 and 6 show bending curves of initial and recovered samples for CF/PET sandwiches and CF/Epoxy sandwiches. In both cases, one sample was tested after recovery without applying the self-healing function. CF/PET sandwiches showed a good repeatability in terms of stiffness and strength of initial samples. As expected, in the case of epoxy foam core, the sample with the SMC skins (referred as Sample III in Figure 6a) showed higher mechanical performances because of the higher distance between the plies of the composite skins.

![CF/PET sandwich](image1)

![Epoxy/PET sandwich](image2)

Figure 4: Failure of SMC sandwiches with PET (top) and epoxy (bottom) foam core.
Figure 5: Bending curves of CF/PET sandwiches before (damage) and after (post-recovery) shape recovery in absence (left) or presence (right) of the self-healing function.

Figure 6: Bending curves of CF/Epoxy sandwiches: a) initial tests on sandwiches without (Sample I and Sample II) and with (Sample III) SMC skins; b), c), and d) bending tests before and after recovery for Sample I (without self-healing function), Sample II (with self-healing function) and Sample III (with self-healing function and SMC skins), respectively.
4 DISCUSSION

Both commercial PET foams and home-made epoxy foams by solid state foaming have pronounced shape memory properties. Large damages can be easily recovered by heating at least in terms of shape. The effect of the self-healing function is also quite evident, particularly in the case of CF/Epoxy sandwiches. In order to quantify this effect, Table 1 reports stiffness data extracted from bending curves of all the sandwiches before and after recovery (Figure 5 and 6). Residual stiffness after recovery is a simple way to measure the efficiency of shape recovery and self-healing. Strength could be used as well but several failure mechanisms were observed during tests and it is difficult to make a comparison.

<table>
<thead>
<tr>
<th>Sandwich type</th>
<th>Details</th>
<th>Initial stiffness (N/mm)</th>
<th>Stiffness after recovery (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF/PET</td>
<td>No healing</td>
<td>139.6</td>
<td>56.8</td>
</tr>
<tr>
<td>CF/PET</td>
<td>Healing</td>
<td>124.7</td>
<td>99.6</td>
</tr>
<tr>
<td>CF/Epoxy</td>
<td>No healing</td>
<td>664.4</td>
<td>124.8</td>
</tr>
<tr>
<td>CF/Epoxy</td>
<td>Healing</td>
<td>493.3</td>
<td>623.0</td>
</tr>
<tr>
<td>CF/Epoxy</td>
<td>Healing + SMC skins</td>
<td>797.9</td>
<td>720.3</td>
</tr>
</tbody>
</table>

Table 1: Stiffness of SMC sandwiches before and after recovery.

After shape recovery of CF/PET sandwiches, if the self-healing function is not added, a residual
stiffness about 41% is measured. Taking into account the kind of damage (i.e. the composite skin break), it is not a low value in absolute terms. However, the residual stiffness in the case of healing is much higher (80%). If the self-healing function is added to this kind of composite sandwich, after recovery it behaves in a way more similar to the sound composite than the damaged one.

CF/Epoxy sandwiches showed higher stiffness because of the higher core density and properties. On the other hand, the foam core was more sensitive to cracks under bending. Due to this fact, very low residual stiffness was measured in the sample without the self-healing function (19%). Moreover, also the effect of the self-healing function is stronger. In the case of using SMC skins, a 90% of residual stiffness was observed. In the sample with the healing function but without the SMC skins, the residual stiffness was even higher than the initial one (+26%).

5 CONCLUSIONS

Using SMCs in marine applications could lead to the production of self-healing structures. Typically, self-healing works at room temperature and composites are fixed in the damaged configuration. This fact can originate the loss of functionality of the composite part. The best thing should be recovering shape and partial performances of composite structures so that they can continue to carry out their function. In this way, SMCs seem to be optimal. In fact, their shape can be recovered by heating and the self-healing function can be added to repair the damage. Attention has to be paid in using self-healing resins which can be activated in temperature. As a result, shape recovery and damage recovery can be achieved contemporarily in a short time.

Present study is the proof of concept for the combination of shape recovery and self-healing. The self-healing function has been simulated by using a liquid resin after composite damage. Results are promising and seem to confirm the validity of this approach. Sandwich structures are particularly suitable for producing SMC structures with self-healing properties because of the possibility of using SM foams for core. In the study, only commercial materials have been used with the evidence of high residual properties after shape and damage recovery. It has also been shown that it is possible to concentrate the shape memory behavior only in the foam core, leaving the composite skins made of traditional materials.

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REFERENCES

