

DEVELOPMENT OF A PROCESS WINDOW FOR DEBONDABLE ADHESIVES IN HIGH PERFORMANCE AEROSPACE APPLICATIONS

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ABSTRACT

Composite materials, particularly sandwich structures with carbon fibre reinforced skins, are known for their exceptional bending stiffness. However, they present significant challenges in terms of end-of-life recycling due to the difficulty of separating their constituent materials. Improvements are needed to advance circular economy practices and support decarbonization targets. To address this issue, a novel interfacial primer has been developed to enable the controlled separation of layers in multi-material composites, facilitating targeted recycling of individual constituents. The primer contains thermally expandable polymer microspheres in a carrier fluid. Upon thermal activation, expansion of these spheres weakens the interface enabling low peel stress separation at room temperature of the constituents. The spheres retain their integrity during the composite cure under high temperature and pressure and are compatible with one-shot manufacturing processes such as autoclave processing. The primer was formulated for high-performance applications, including systems with glass transition temperatures above 135°C. Primer constituents and the subsequent process window were characterized using mechanical tests, including Single Cantilever Beam (SCB), flatwise sandwich tensile testing and single lap joint testing; combined with optical and electron microscopy. By following defined processing guidelines, efficient end-of-life debonding (<0.5 MPa) could be achieved at room temperature, paving the way for separation of core and skin structures to give recycle streams that increase yield during recycling processes thereby enhancing composite life-cycle management.

1. INTRODUCTION

Composite sandwich structures are widely adopted in various industries including aerospace, automotive, energy and infrastructure, for their high weight specific mechanical properties. However, the separation, recycling or repair of such structures remains a major drawback when assessing the life cycle of these materials. To address these issues, the use of debondable adhesives have been proposed to allow thermoset reinforced resins to be separated from other substrates¹ such as a sandwich core material. Hence the two materials can then be recovered and recycled in different processes, each optimized to the relative constituent material (for example different variants of solvolysis or pyrolysis), increasing yield or molecular integrity of the recovered products and thereby enhancing circularity and lowering the total product carbon footprint. The triggering of de-bonding can be achieved on demand by means of different stimuli, without interfering with the materials properties and ply to core interface during the product life cycle. These triggers can be heat, light, pH change, electric, magnetic or ultrasound and should be selected considering the limitations of materials compatibilities². With the recent development of covalent adaptable networks (CAN), reversible chemistries were introduced in thermoset adhesives that can be debonded on demand³⁻⁵. Other studies focused on the integration of sacrificial layers where separation of layers is desired, through thermal degradation⁶, expandable microspheres^{7,8} or shape memory alloys⁹. With a potential to be used in any multi-layered materials, de-bondable adhesives may provide a suitable pathway towards sustainable maintenance and recycling. It is known that the constituent raw materials often form a majority of the carbon footprint of products, even more so as the electricity mix of modern and developed countries is decreasing its greenhouse gas emission year after year. The reduction of waste and the re-use of materials is thus a crucial point to address. In composite parts, where several layers contain various materials, effective separation of these components can significantly improve the quality of the recycling streams and allow better recovery of the constituents for a second life cycle. Yet, the debondable adhesive layer should survive the

temperature and pressure during the curing process and should not compromise the service properties and durability of the part.

In this project, a sandwich structure is used as a demonstration case in an aerospace application, where skins are composed of Carbon Fiber Reinforced Polymer (CFRP), and the core is a lightweight polymer foam. In traditional sandwich composites, permanent thermoset adhesives hinder the separation of the layers and recycling. Currently, the end-of-life management of composite sandwich structures is limited to mechanical or thermal recycling, where materials are ground into granulates and reused as low-value fillers or incineration with partial energy recovery. In both cases, the material loses its initial structural and functional properties and loses all possibility of circularity. CFRP parts without core materials can be more readily recycled and the carbon fiber recovered using pyrolysis and the resin can also be recovered using solvolysis processes. The different chemistries of the epoxy matrix in the CFRP and the foam or core materials used significantly complicate the recycling process.

The objective of this work is thus to evaluate the possibility to separate the skin from the core after the end of life of the part, while keeping the processing and the structural integrity equivalent to those for the benchmark epoxy bonded sandwich structure. We thus introduce debondable primer formulations containing expandable microspheres and develop a process window that maintains mechanical properties during the application service life, and which enables disassembly at the end of life thereby facilitating recovery of the high-value CFRP skin and core components. By carrying out thermomechanical analysis on the primer in different time and temperature conditions, processing windows are established. These processing conditions vary according to the composite processing conditions, but also according to the substrate characteristics such as the surface roughness. Once the optimal processing conditions are set, different thermomechanical tests are used to validate these windows, such as CFRP/CFRP lap shear tests, Single Cantilever Beam tests (SCB)¹⁰, and flatwise tensile tests.

2. RESEARCH TESTS & EXPERIMENTS

2.1 Materials

To manufacture composite parts containing the debondable layer, the CFRP skins are composed of a carbon fiber 200 gsm 2x2 twill reinforced bio-attributed mass-balanced epoxy resin pre-preg, supplied at a sample scale by Huntsman. The core is a PMI Rohacell foam 51WF from Rohacell, with samples as used in the incumbent product supplied by Pilatus Aircraft. Finally, the debondable primer was supplied by Huntsman which consists of thermally expandable microspheres (TEM) diluted in a mixture of thermoplastic binder in isopropyl alcohol. The TEM are thermoplastic capsules that contain hydrocarbon fluid. Upon thermal activation, the hydrocarbon vaporizes, and the gas expands the softened thermoplastic shells, as illustrated in Figure 1. The grade of polymer in the binder, the TEM thermoplastic shell material, and the hydrocarbon composition influence the softening temperature and expansion conditions.

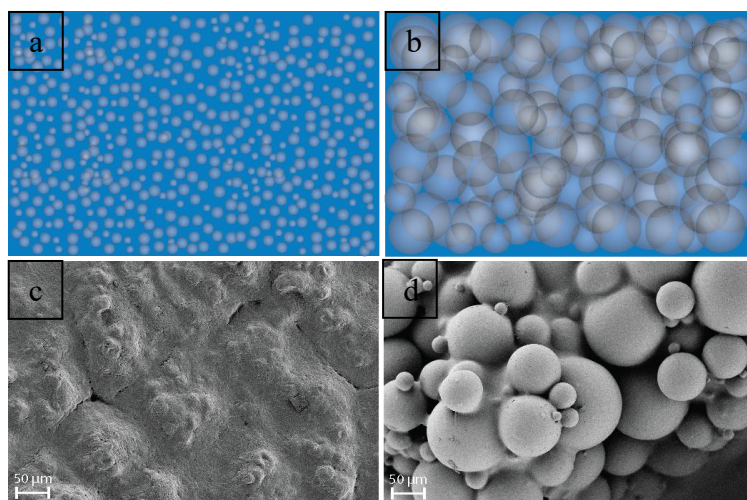


Figure 1 - Schematic (a,b) and scanning electron microscopy (c,d) images of the virgin (a,c) and expanded (b,d) microspheres contained in their polymeric carrier.

2.2 Experimental methodology

The preparation of CFRP composite parts using a debondable primer layer starts with the preparation of a homogeneous film of constant thickness using a doctor blade setup as illustrated in Figure 2. Precision micrometers enable the wet film thickness to be accurately selected. Knowing the amount of solvent that evaporates in the solution, it is then possible to prepare dry films of a precise thickness. Once the solvent is evaporated, the film can be manipulated and placed at the interface that should be debonded, the CFRP/CFRP interface or the CFRP/core interface. Note that this step is not necessarily adapted to a realistic part production, where brushing or spraying of the primer may be preferable, but was necessary to ensure a precise amount of primer for the small-scale laboratory tests. The part is then manufactured following standard lay-up procedures for pre-preg curing in an autoclave, and resin curing is achieved with a cycle at 2.5 bars, and 130°C according to resin manufacturer and part producer recommendations. Following curing, the samples are cut to the desired dimensions using a mechanical table saw.

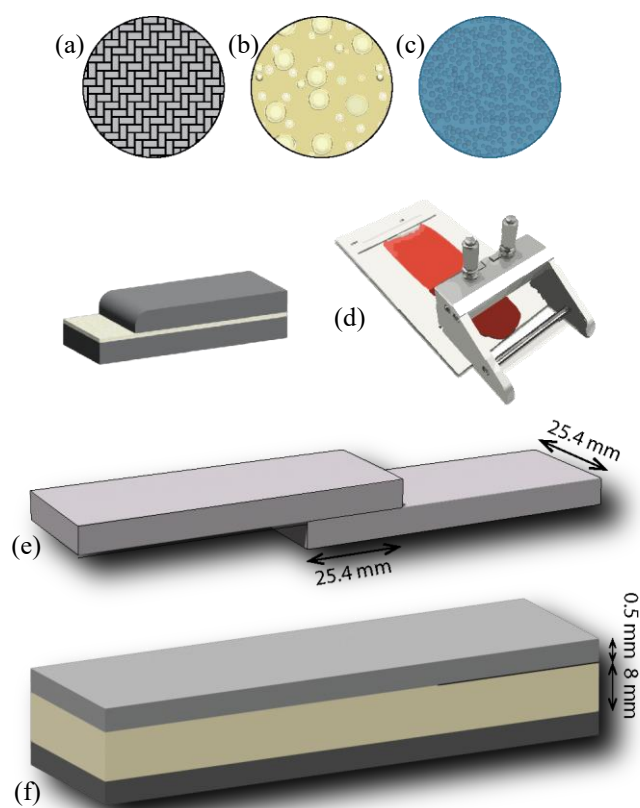


Figure 2 – Schematic representation of the composite manufacturing, using the CFRP prepreg (a), the foam (b) and the debondable primer film (c) – prepared with a doctor blade setup (d). A single lap shear sample (e) as well as a sandwich panel (f) are represented.

Several formulations were prepared with primer films of different thicknesses and containing different concentrations and grades of TEM for tuned debonding applications. One first primer debonds at 150°C and is therefore called P150, while the second one has a debonding temperature around 170°C and will be referred to as P170. Having different grades and concentrations of TEM can offer a variety of debonding driving interfacial pressure and under different conditions.

Thermal characterization of the primer was first assessed alone, using optical and electronic microscopy, for observation of TEM expansion under various conditions. The morphology, size distribution and shell thickness were also studied. In parallel, thermal activation was studied using DSC and TGA, both at a rate of 10 °C/min. The melting points and thermal degradation onsets were identified for each component of the primer.

Then, DMA Q800 – TA Instruments – was used in compression mode to record the strain due to expansion while applying a constant force, in isothermal conditions and dynamic ramps. The volumetric expansion could then be

plotted for different temperatures as a function of time. These tests determined the outer limits on conditions that should not be met during manufacturing and service life if debonding should be achieved.

3. RESULTS

Figure 3 shows the results of isothermal tests performed on the P150 and P170 dry films. The gap first decreases as explained by the softening of the thermoplastic shells above $\sim 120^{\circ}\text{C}$. Following this, the expansion starts and gets more intense as the temperature is close to the theoretical expansion temperature.

These results suggest that pre-mature expansion happens for both grades of primer, which limits the possibility to expose parts to high temperatures before the end-of-life. The results also show that expansion takes more time when the temperature is lower and is limited in duration. This could happen because the hydrocarbons leak out from the shells when these are soft enough. The expansion, to be efficient and complete should therefore happen quickly (in the order of 1-5 min) at the selected (high) temperature. On the other hand, curing should not take place at too high temperature, as this could pre-trigger microparticles, and then hinder a full expansion when desired.

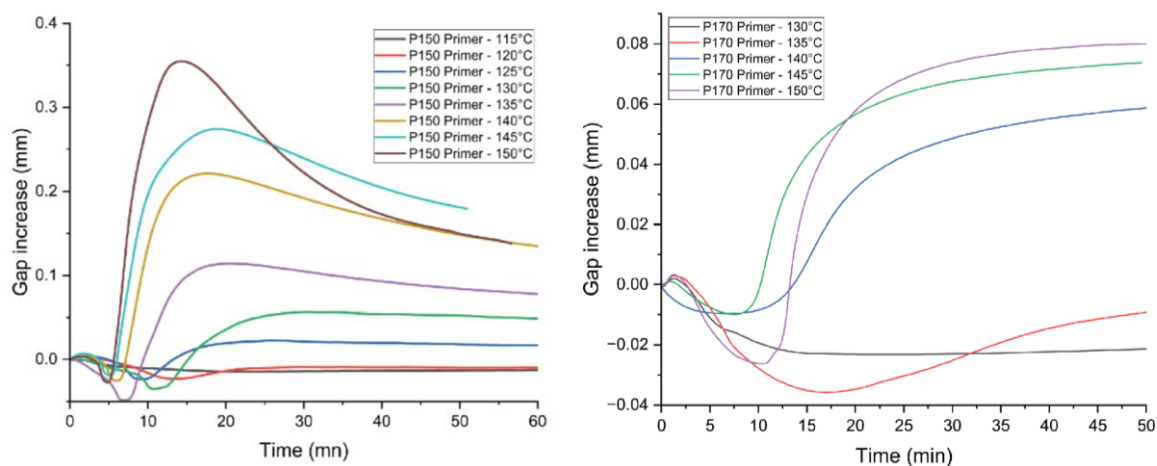


Figure 3 – Isothermal strain measurements in DMA for P150 and P170 primers.

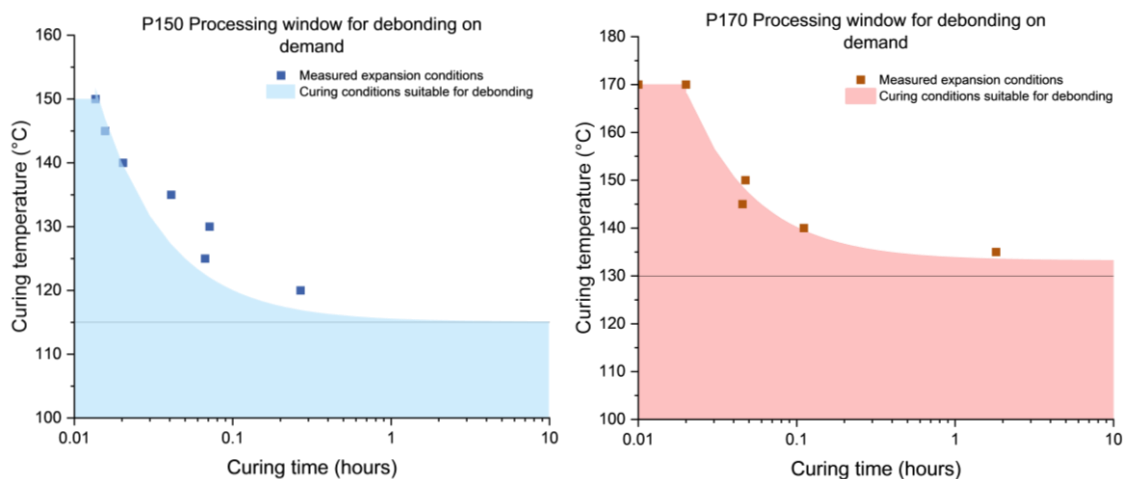


Figure 4 - Processing windows of the CFRP composite materials for debonding on demand using P150 and P170 primers, based on real data measurements.

Figure 4 presents the processing windows for both P150 (left) and P170 (right) primers. The colored regions indicate the processing conditions under which composite manufacturing can be carried out while still enabling

separation of the layers through primer expansion. It can be observed that curing time significantly influences the expansion behavior of the TEM. In addition, the results demonstrate that a minimum temperature gap between the resin curing temperature and the primer's theoretical expansion temperature is required. For both grades studied, a difference of approximately 40°C is necessary, particularly for long curing time (e.g. > 1 hour). Moreover, depending on the substrate, experimental observations revealed that higher TEM loadings are required in core materials with large pore volumes especially on the CFRP to core interfacial surfaces, such as low-density polymer foams. In these cases, the expanding TEM initially fill the large cavities, before initiating debonding at the thermoset interface. The separation of layers is facilitated by the softening of the binder above its melting point, which enables the TEM shells to expand under internal gas pressure. Reaching the glass transition temperature of the thermoset matrix can further promote interface opening.

Following this analysis, the debondable primer concept was applied to assess mechanical performance and verify comparability with standard composite layouts. Thermo-mechanical characterization confirmed that the debondable primer does not compromise initial bonding properties. Single lap shear tests showed that both primed and unprimed systems exhibited lap shear strengths of approximately 23.6 ± 3.2 MPa and 21 ± 0.5 MPa respectively, which decreased to about 0.5 MPa after thermal activation of the primer. For sandwich structures, flatwise tensile tests revealed that virgin samples with primer displayed lower tensile strength than unprimed samples (0.9 MPa vs 1.3 MPa), but also decreased below 0.5 MPa after thermal activation at 170°C. The lower initial tensile strength of virgin primed sandwich structures is attributed to the high TEM concentration in the primer required to fill the foam pores and achieve complete debonding, which results in a weaker interface. When denser foams are used in sandwich structures, this TEM loading can be reduced, thereby improving initial strength, while ensuring effective separation of the layers when desired. However, results of SCB demonstrated that debonding by peeling the skin off the foam is facilitated by having a primer layer and prevents foam breaking. This results in a neat interface with only foam and primer residues on one side and the CFRP skin on the other side, as illustrated on Figure 5. Overall, mechanical testing confirmed a pronounced loss of adhesion after activation.



Figure 5 – Flatwise tensile test samples showing (a) a sample without primer with rupture within the foam; (b) samples with 30 gsm P170 primer virgin (bottom) and heat activated (top); (c) samples with 60 gsm P170 primer virgin (bottom) and heat activated (top).

This study demonstrates that activation conditions can be tuned to balance service stability with controlled debonding. Depending on the substrate and application, both the concentration and grade of TEM in the primer can be adjusted to optimize the trade-off between the mechanical integrity during service and efficient separation upon activation.

Controlled debonding provides a pathway to improve recyclability and circularity of multi-materials systems, contributing to a Net-Zero composites industry. By demonstrating scalability to industrial processes and clarifying the expansion kinetics, this work shows the potential for designing and manufacturing large and complex composite parts with the aim of recovering, recycling and reusing the constituent components. Achieving this

requires tailored primer formulations, specifically the type and loading of TEM contained in the binder, to reach an optimal between high performance and effective end-of-life separation.

4. ACKNOWLEDGEMENTS

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