SURFACING AND LIGHTNING STRIKE PROTECTION OF BISMALEIMIDE COMPOSITES WITH A NOVEL HIGH TEMPERATURE SURFACING FILM

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ABSTRACT

Bismaleimide (BMI) adhesives and prepregs are key materials for aerospace structures due to their high temperature capabilities and chemical and environmental resistance compared to their epoxy counterparts. In some applications, where BMIs are predominately utilized for their high Tg and mechanical properties, there is also a need to provide good surface quality and lightning strike protection (LSP). While epoxy based films for surfacing and LSP are very prevalent in the industry, there are minimal options available for BMI composite structures. In this paper, a novel BMI-based composite structure that provides excellent surfacing, fluid resistance and LSP will be discussed. The potential for incorporating lightweight surfacing films into BMI composites for surfacing and LSP in high temperature applications will be demonstrated.

Keywords: Bismaleimide, Surfacing Films, High Temperature, composites

1. INTRODUCTION

Composite materials are increasingly utilized in high performance aerospace applications due to the growing demand of OEMs to create lighter, faster and more cost efficient aircraft. While the use of composite materials has many advantages, one drawback is the potential for increased surface imperfections compared to metal, which can add steps to the manufacturing process, such as multiple sanding and filling cycles to achieve a paint ready aircraft surface. Consequently, the process to prepare a composite surface for painting can be very labor intensive and time consuming. Fortunately, this process can be alleviated with the use of a surfacing film co-cured with the prepreg as the outermost layer during assembly[1]. The use of a surfacing film can reduce the part manufacturing time associated with surface preparation by eliminating surface imperfections such as pin holes, pits and porosity. A surfacing film could offer the potential to provide a high quality, smooth surface that is ready for priming and painting. Additionally, surfacing films can be embedded with metallic foil or screen materials to provide a combination of excellent surface quality and lightning strike protection. The majority of surfacing films on the market today are based on epoxy resin systems. Solvay currently supplies one of the most widely utilized surfacing films in the aerospace industry, SURFACE MASTER® 905 (SM 905)[2]. Epoxy based surfacing films can be successfully utilized at a temperature range of 250ºF to 350ºF. These films are primarily used in aerospace applications for fuselage, wings, tails and other composite based parts where surfacing is required with thermal requirements less than 350°F. An example of where surfacing films are utilized on an aircraft is shown in Figure 1.

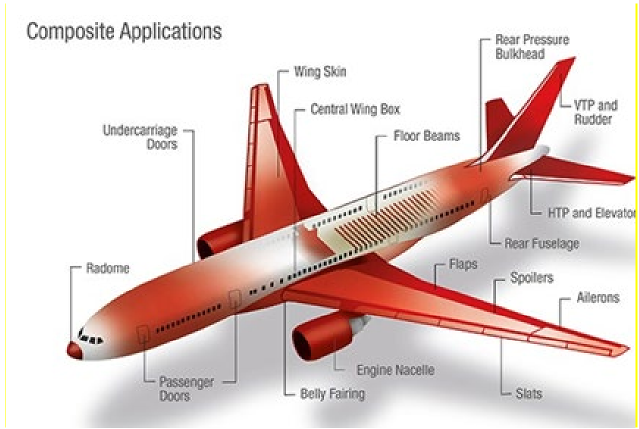


Figure 1. Current Surfacing Film Usage in Composite Aerospace Applications[3]

One need that still exists, in the realm of aerospace surfacing films, is a surfacing film that can withstand higher temperatures (>350ºF) and can provide better co-cure compatibility with bismaleimide prepregs, which commonly require a high temperature post cure, not suitable for epoxy-based materials. It is well known that the use of BMI resin systems in adhesives and prepregs yield products with higher temperature performance and stability than their epoxy counterparts. However, to our knowledge, there is no commercial BMI resin based surfacing film capable of providing high surface quality and LSP functionality. The goal of this work was to investigate the use of BMI resins and their subsequent co-reactants to develop a BMI surfacing film that meets all surfacing film requirements for high temperature applications.

2. EXPERIMENTATION

2.1 Materials

For the current study, the BMI-based thermoset prepreg system CYCOM® 5250-4 fabric prepreg from Solvay was utilized as the substrate material. The developmental BMI surfacing film was manufactured at Solvay and coated at various film weights with a glass carrier. For the control work, the epoxy-based thermoset prepreg system, CYCOM® 5320-1, from Solvay was utilized as the substrate material and co-cured with Solvay's SURFACE MASTER® 905 surfacing film.

2.2 Lay-up and Processing

The composite laminates were prepared by laying up 6 plies of CYCOM® 5250-4 consolidated in the following direction: 0º/90º/0º/90º/0º/90º. A vacuum debulk was performed every 2 plies. To prepare the composite surfacing panel for autoclave curing, the BMI surfacing film (with carrier and metallic screen or foil, as specified) was placed resin rich side to a tool coated with Frekote. On top of the surfacing film was then placed 6 plies of CYCOM® 5250-4. The lay-up scheme for the BMI surfaced composite structure is shown in Figure 2.

Figure 2. BMI Surfacing Film Lay-up with BMI Prepreg

The layup was then cured by heating at 3°F/min to 250°F followed by a 45 min hold at 250°F under 15 psi pressure. The pressure was then increased to 85 psi followed by a 3°F/min ramp to 350°F and held for 360 min. The cured panel was then post-cured in an oven for 360 min at 440°F. Control panels of SURFACE MASTER® 905 were prepared using the layup method above with CYCOM® 5320-1.

2.3 Thermal Analysis

Thermomechanical Analysis (TMA) was used to determine the glass transition temperature of the samples using a TA Instruments TMA Q400 at a ramp rate of 10ºC/min from RT to 350ºC. Thermogravimetric Analysis (TGA) was performed using a TGA Q50 (TA Instruments) on the cured surfacing film to determine the thermal stability with a ramp of 10°C/min to 500°C.

2.4 Optical Microscopy

Digital microscope images of the composite surfaces was performed using a Keyence VHX-2000E 3D digital microscope.

2.5 Scanning Electron Microscopy

SEM analysis was conducted using a Hitachi S-4800 microscope at various magnifications.

2.6 Infrared Spectroscopy

FT-IR spectra were recorded on a Thermo Scientific Nicolet iZ10 FT-IR. An average of 16 scans was recorded for each run at room temperature.

2.7 Paint Stripper and Hydraulic Fluid Analysis

Cured BMI surfacing panels were cut into 2 inch by 2 inch samples and tested for initial weight and pencil hardness. The samples were then soaked in Cee-Bee Paint Stripper E-2012A or Skydrol B4 Hydraulic Fluid and retested for weight gain and pencil hardness each day for one week.

3. TECHNICAL APPROACH AND STRATEGY

Currently, epoxy based surfacing films, such as Solvay's SURFACE MASTER® 905, are perfectly positioned for applications such as fuselage, wings and tails where service temperatures up to 350°F are required. While SM 905 is ideal for these applications, there is currently a need in the aerospace market for a surfacing film that can withstand high temperature applications (>350°F). This high temperature surfacing film technology would be ideal for military, defense, space, and supersonic applications, as well as additional opportunities in civil aerospace. While there are various resin systems that can be chosen that exhibit higher service temperatures than epoxies, bismaleimides are known to yield higher thermal and mechanical properties, as well as exhibit similar processing properties to their epoxy counterparts, Figure 3.

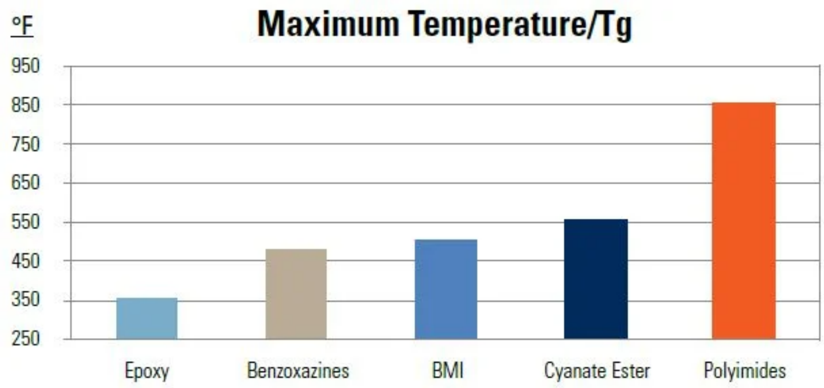


Figure 3. Service Temperature of Common Aerospace Resins[4]

Therefore, in order to increase the thermal performance properties of the new surfacing film, various BMI monomers were trialed. One drawback of the use of BMI resins is their propensity to create strong, but brittle cured networks. To overcome this issue, various allyl and propenyl comonomers were incorporated and tested for their toughening effect on the resin system. In addition to the monomers, multiple fillers and pigments were incorporated to tailor the color, surface appearance and handling of the film. The best combination of BMI monomers and comonomers that yielded high temperature performance and good handling and processing was down selected for additional analysis to probe the surfacing, appearance and critical fluid requirements common for the testing of surfacing films.

4. RESULTS

4.1 Surfacing Film Appearance and Surface Quality

As discussed above, one challenge with the use of composite materials is the ability to obtain a high quality, robust surface finish. It is evident that without a surfacing film, composites have an uneven surface appearance, which would make surface preparation and painting challenging, therefore requiring additional sanding and filling steps at an OEM shop floor. This trend is observed for virtually all composites without the use of a surfacing film. For example, CYCOM® 5250-4 prepared without the use of a surfacing film, Figure 4, exhibited some surface defects.

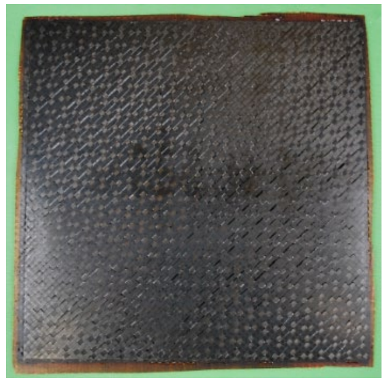


Figure 4. Control CYCOM® 5250-4 Fabric Without Surfacing Film

In parallel, CYCOM® 5250-4 was laid up and cured with the incorporation of the developmental BMI surfacing film containing metallic screen or foil. These surfaced composite structures were cured and then examined for the appearance of surface porosity, pin holes or pits. All cured BMI surfaced composite panels produced surfaces with excellent quality and appearance with no observable porosity, pits or pin holes at film weights ranging from 0.025 psf to 0.040 psf. The surfaces were examined before and after post cure, Figures 5 and 6, respectively. It should be noted that, visually, the surface color of all panels slightly darkens after undergoing the 440˚F post cure. However, this slight discoloration after post cure is not an issue as there were no detrimental effects to the surface quality or the thermal properties. This observation was confirmed by the use of Infrared spectroscopy, Figure 7, which was performed on the BMI surfaced composite after autoclave curing and then following additional post cure. The spectra are overlaid to show no distinct changes. The key features for bismaleimides are observed in both spectra such as the imide stretch at ~1710 cm^{-1} and bands associated with CNC and CN stretching at ~1300-1500 cm^{-1}.

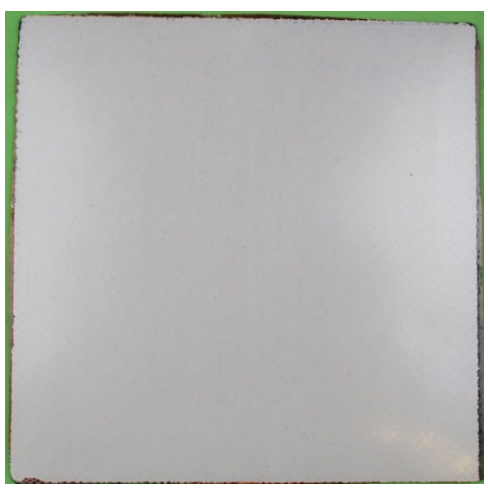


Figure 5. BMI Surfaced CYCOM® 5250-4 Composite Structure (Autoclave Only Cure)

Figure 6. BMI Surfaced CYCOM® 5250-4 Composite Structure (Autoclave + Post Cure)

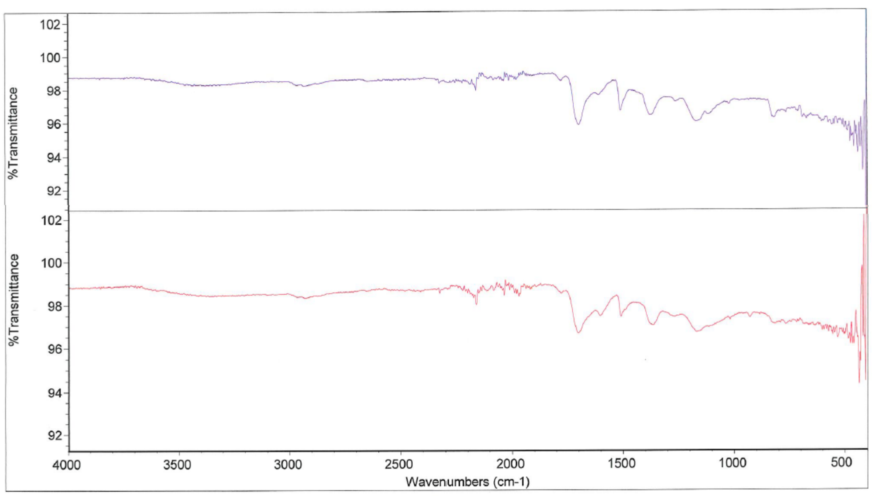


Figure 7. Infrared Spectra of BMI surfaced CYCOM® 5250-4 Autoclave Cure (Top/Purple) and Autoclave + Postcure (Bottom/Red)

4.2 Surface Analysis of BMI Surfaced Composite Structures

To complement the visual inspection of the composite panels, the effect of a BMI surfacing film on the composite structure surface quality was also examined under high magnification using a 3D microscope and by using scanning electron microscopy (SEM). Control CYCOM® 5250-4 and BMI surfaced composite panels were examined before and after the 440˚F post cure. One goal from the surface analysis work was to more closely examine the microstructure for any defects, such as pits, pinholes and roughness. The 3D microscope image and 3D topography profile of CYCOM® 5250-4 with no surfacing film are shown in Figures 8 and 9. The 3D image shows a woven fabric surface that appears uneven. The 3D profile confirms this result with the appearance of multiple peaks and valleys across the image. The surface is not uniformly flat and has many irregularities, which reinforces that painting this uneven surface could be challenging without the use of a surfacing film.

Figure 8. 3D Microscope Image of CYCOM® 5250-4

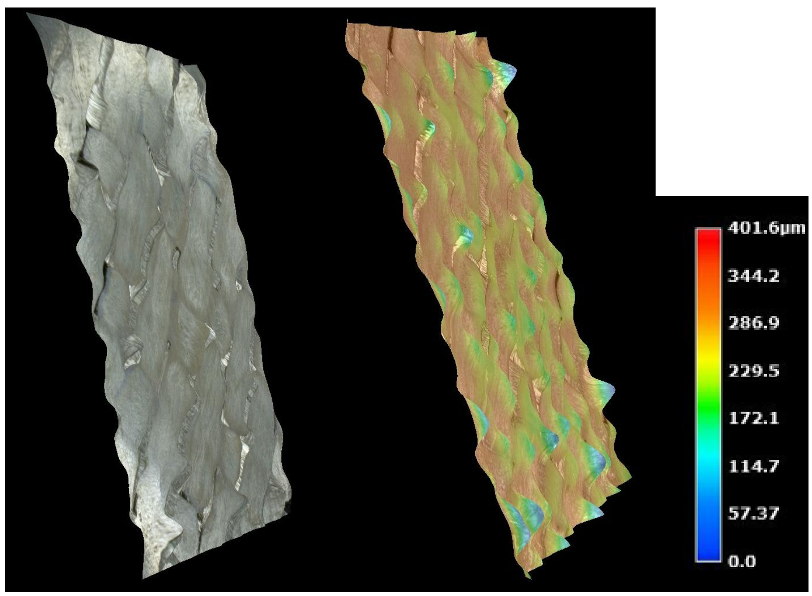


Figure 9. 3D Surface Topography of CYCOM® 5250-4

Additionally, 3D microscope images were taken of the BMI surfaced CYCOM® 5250-4. The images, Figures 10 and 11, show smooth surfaces with a good surface quality at high magnifications with no excessive defects. The small specs observed in the 3D microscope film images are representative of filler particles and are normal to be observed at this magnification given the particle size. These specs do not affect the continuity or smoothness of the films. Additionally, the 3D profile, Figure 12, also confirms that the surfaced composite has a much reduced area of surface roughness and irregularity. It displays a much smoother surface topography compared to the unsurfaced CYCOM® 5250-4.

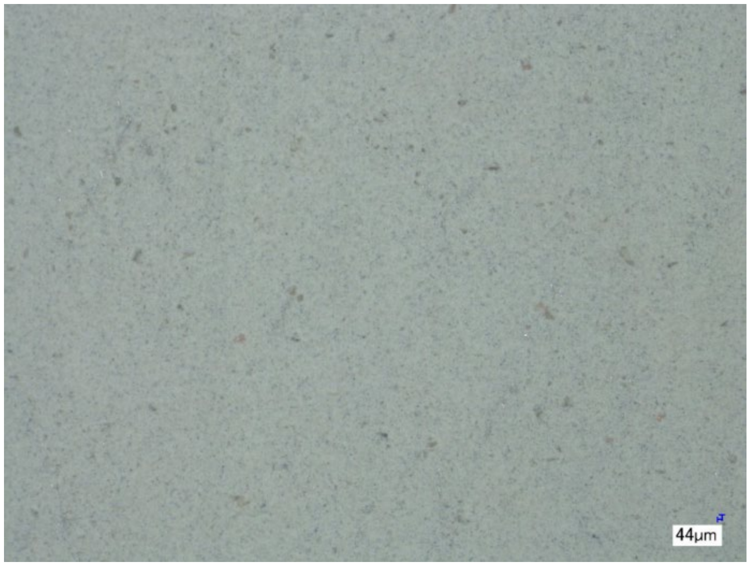


Figure 10. 3D microscope Image of BMI Surfaced CYCOM® 5250-4 Composite Structure (Autoclave Cure)

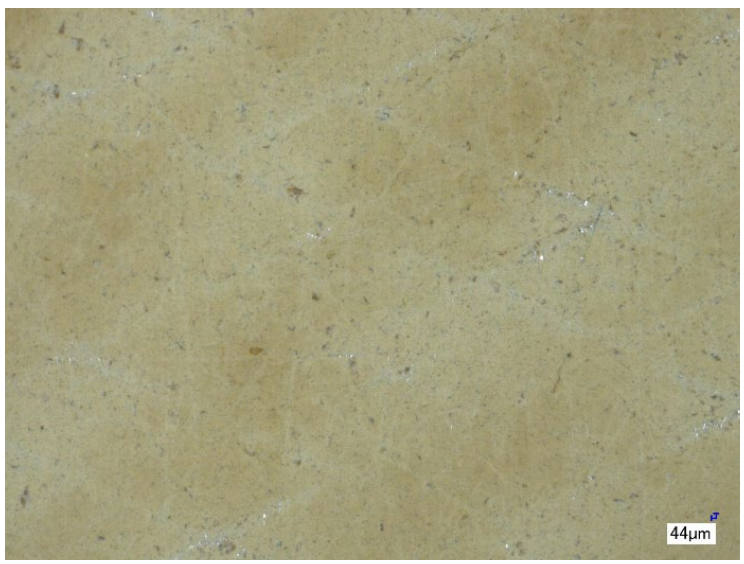


Figure 11. 3D microscope Image of BMI Surfaced CYCOM® 5250-4 Composite Structure (Autoclave Cure + Post Cure)

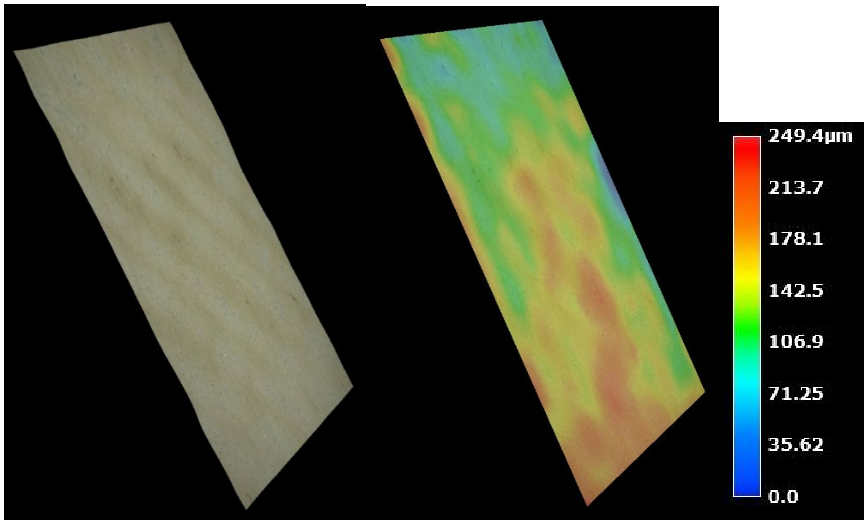


Figure 12. 3D Surface Topography of BMI Surfaced CYCOM® 5250-4

SEM analysis was also utilized to achieve a higher resolution image of the BMI surfaced microstructure after both autoclave cure and post cure, Figures 13 and 14. These images again show a smooth film, with a low level of surface roughness. The slight roughness observed in the microstructure of the 10,000K SEM images is reasonable at this magnification level. The roughness is typical for any resin at this magnification and simply is a result of the different grain crystal sizes.

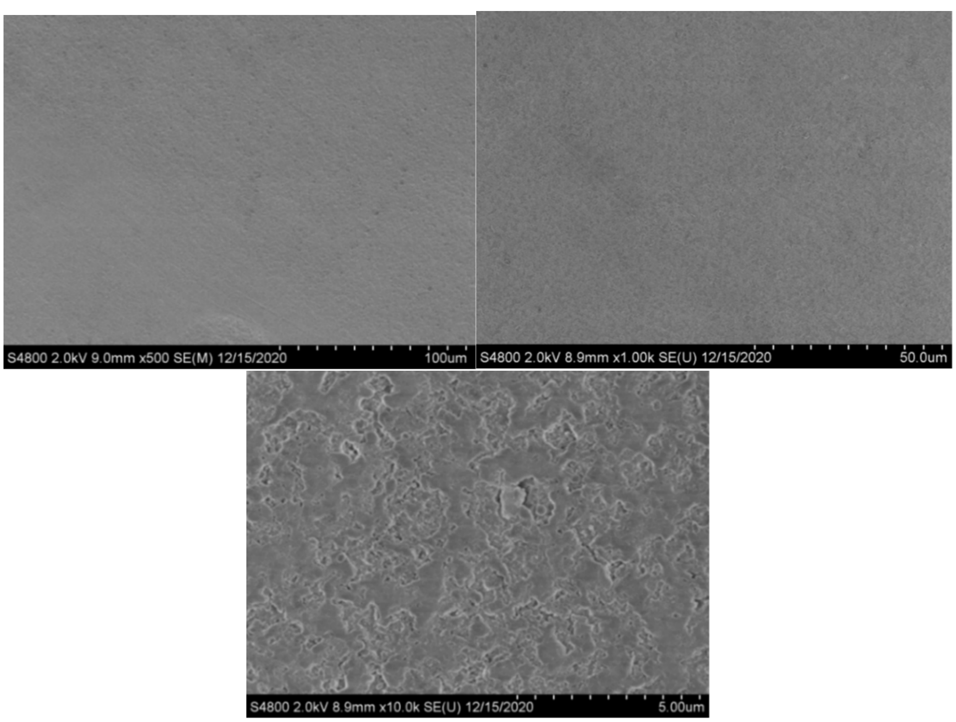


Figure 13. SEM Images of BMI Surfaced CYCOM 5250-4 Composite Structure Autoclave Cured (500, 1000K and 10,000K magnification)

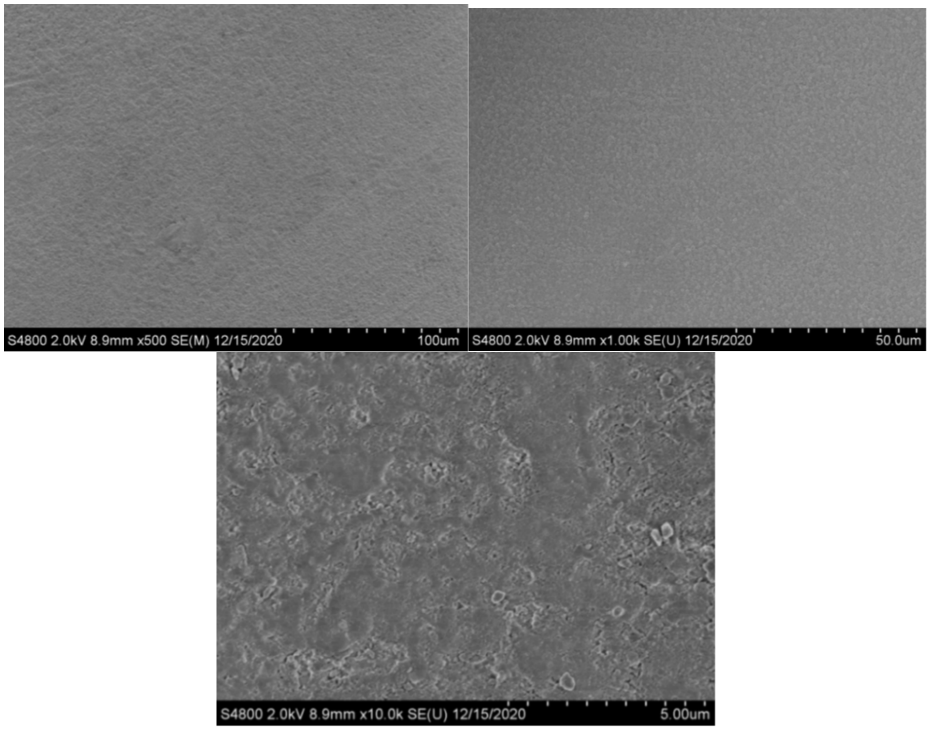


Figure 14. SEM Images of BMI Surfaced CYCOM 5250-4 Composite Structure Autoclave + Post Cure (500, 1000K, 10,000K Magnification)

4.3 Thermal Analysis

The high temperature properties of the BMI surfacing film were explored with the use of thermal analysis and compared to SM 905 per ASTM E2550-17. The glass transition temperature (Tg) of the surfacing films was determined by TMA, Figure 15.

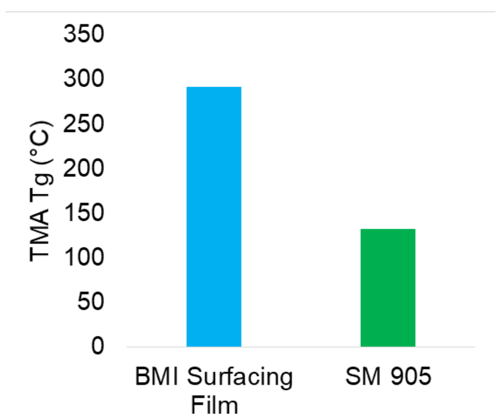


Figure 15. TMA Tg of BMI Surfacing Film vs SM 905

The Tg of SM 905 falls into the anticipated range for epoxy based surfacing films. The development of the high temperature BMI surfacing film, which has a Tg of approximately 300°C, allows for new opportunities for the use of surfacing films at aerospace OEMs. The high temperature properties of the films were further reinforced by Thermogravimetric Analysis (TGA) which was used to determine the thermal stability. The information extracted from the TGA curve is crucial when designing materials because it can define what temperatures a material can withstand and still attain its full performance characteristics. Consequently, it can be a great predictor of the service temperatures that a material can endure and still be viable for use. This test is a great indicator of the epoxy versus bismaleimide performance characteristics. The weight loss curves from TGA analysis are displayed in Figures 16 (BMI surfacing film) and 17 (SM 905). The descending curves show the weight as a function of increasing temperature. The onset of mass loss (where the curve begins to downturn), is where decomposition begins in the sample upon heating. On these curves, we defined the thermal stability as the 5% weight loss of the material, which occurred at 390°C for the BMI surfacing film versus 288°C for the epoxy based SM 905, Figure 18. It is evident that the BMI surfacing film can withstand higher temperature environments compared to SM 905 due to the higher temperature that weight loss occurs in the TGA curves. This outcome was expected as was the intent of the use of BMI versus epoxy resin systems to ensure higher service temperatures.

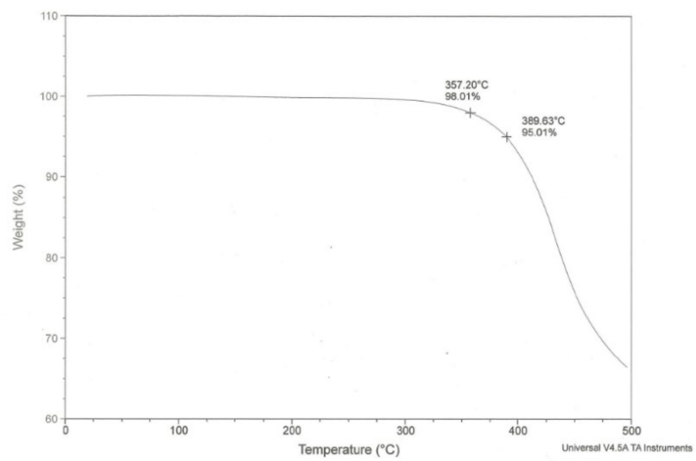


Figure 16. TGA Curve (BMI Surfacing Film)

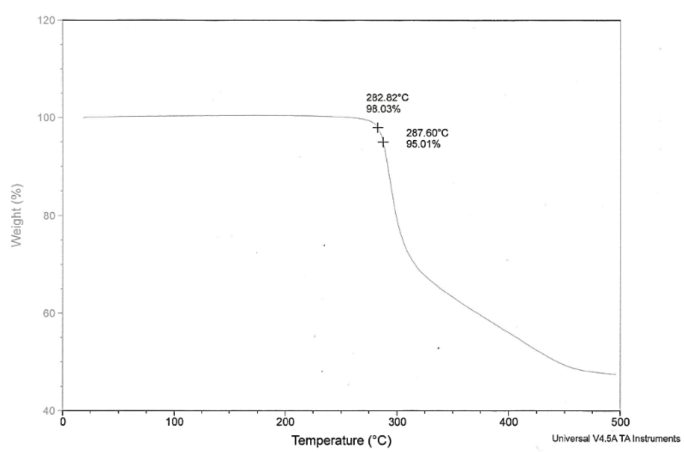


Figure 17. TGA Curve (Surface master® 905)

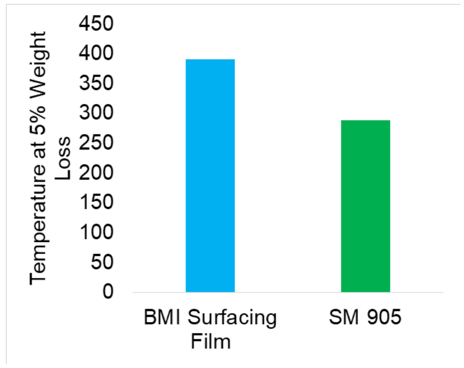


Figure 18. TGA of BMI Surfacing Film vs SM 905 (Temperature at 5% Weight Loss)

4.4 Aerospace Fluid Resistance of the BMI Surfacing Film

An important property of surfacing films, in addition to their appearance, is their resistance to common aerospace fluids such as paint stripper and hydraulic fluid solutions. For this experiment, unpainted BMI surfaced CYCOM® 5250-4 composite panels were cured and cut into 2 inch by 2 inch specimens and immersed in paint stripper (Cee Bee E-2012A) and hydraulic fluid (Skydrol B4) for 1 week at room temperature. The resistance to these fluids was tested by their fluid absorbance (measured by the percent weight gain) and their pencil hardness change over time per ASTM D3363. The pencil hardness should not be reduced by more than 2H pencil grades throughout the course of the testing. All specimens started with a 9H pencil hardness, the hardest level on the pencil hardness scale. Following immersions, the specimens exhibited minimal fluid absorption for paint stripper immersion testing (~0.57% weight gain) and hydraulic fluid immersion testing (~0.30% weight gain). After each immersion study, the films exhibited no film deterioration and no change in the pencil hardness value of 9H from the beginning to the end of the fluid immersions. The results of the testing are displayed in Figure 19.

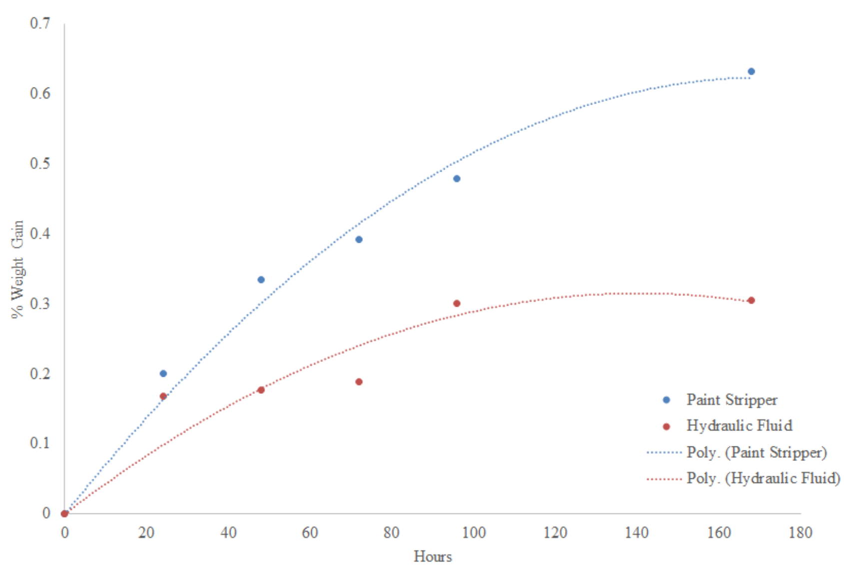


Figure 19. Paint Stripper (Cee Bee E-2012A) and Hydraulic Fluid (Skydrol B4) Absorption over Time

4.5 BMI Surfacing Film Adhesion Properties

In order to find utility in commercial and military aircraft, the BMI surfacing film must exhibit good paint adhesion to allow for priming and painting of the surface. First and foremost, the role of surfacing films in aerospace applications is to reduce the steps needed to achieve a paint-ready aircraft by providing a surface with no imperfections or defects. The assessment of paint adhesion is commonly tested by a crosshatch adhesion tape test, a common customer requirement per ASTM D3359. The rate of adhesion is classified by the following scale, Figure 20. Ideally, no paint removal (a rating of 5B) is preferred.

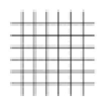
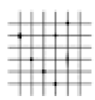
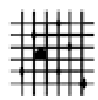
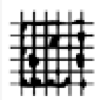
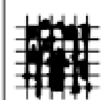
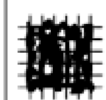
Surface cross-cut area from which flaking has occurred (6 parallel cuts)						
Classification	5B (0%)	4B (<5%)	3B (5-15%)	2B (15-35%)	1B (35-65%)	0B (>65%)

Figure 20. Classification of Adhesion Test Results (per ASTM D3359)

To assess the paint adhesion properties, the BMI surfaced cured composite panels were treated with a standard paint primer and topcoat widely used for aircraft painting applications. Following priming and painting, the adhesion was tested by performing a 45° crosshatch adhesion test (a more rigorous test than the 90 degree crosshatch shown in Figure 20). The ideal outcome of this adhesion test is to observe no paint peel off following the application and removal of pressure sensitive tape at the cross hatch cuts. Following testing, the BMI surfaced composite panels showed excellent paint adhesion with no paint removal upon tape application and removal, Figures 21 and 22. These results match up well to what is observed with epoxy based surfacing films such as SURFACE MASTER® 905.

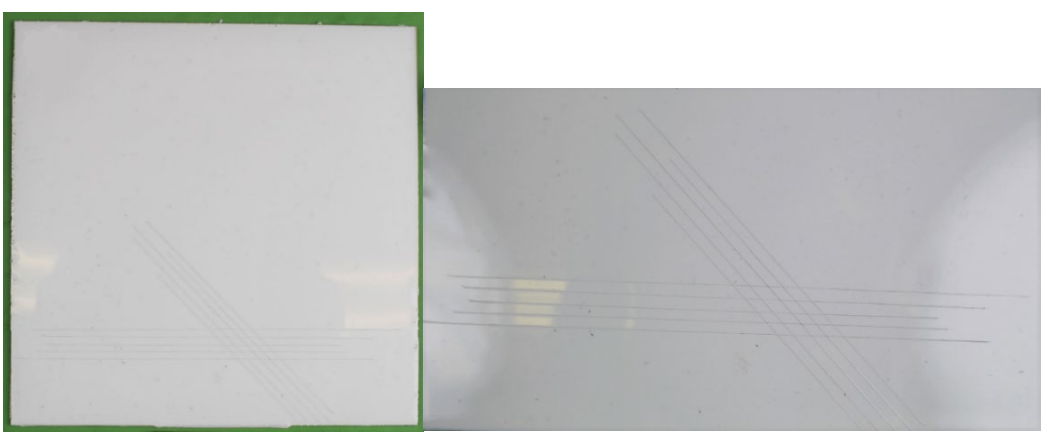


Figure 21. BMI Surfaced CYCOM® 5250-4 Paint Adhesion 45° Crosshatch Testing

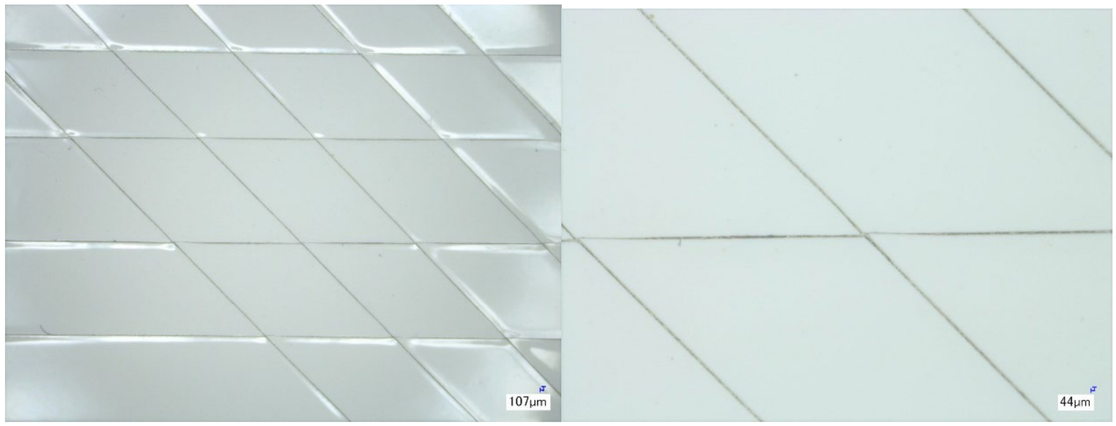


Figure 22. 3D Microscope Images of Crosshatch Showing No Paint Removal

4.6 Lightning Strike Protection Testing

Composite based aircraft generally lack the superior conductivity, and therefore the LSP protection that is inherent in metal based parts of an aircraft. Consequently, there is a need to provide lightning strike protection to composite structures. In recent years, the state of the art for composite aircraft lightning strike protection has been to utilize a highly conductive surfacing film. To mimic the lightning strike damage on a composite structure and to verify the LSP functionality of the developmental BMI surfacing film, BMI surfaced CYCOM® 5250-4 laminate panels were prepared (20 inch x 20 inch size) and sent to Lightning Technology Inc. (LTI) in Pittsfield, MA for Zone 1A (LS test for radome) and 2A (LS test for fuselage) lightning strike testing, Figure 23. This testing is in progress and once completed, the lighting stroke damage will be assessed by visual examination and common NDI methods.

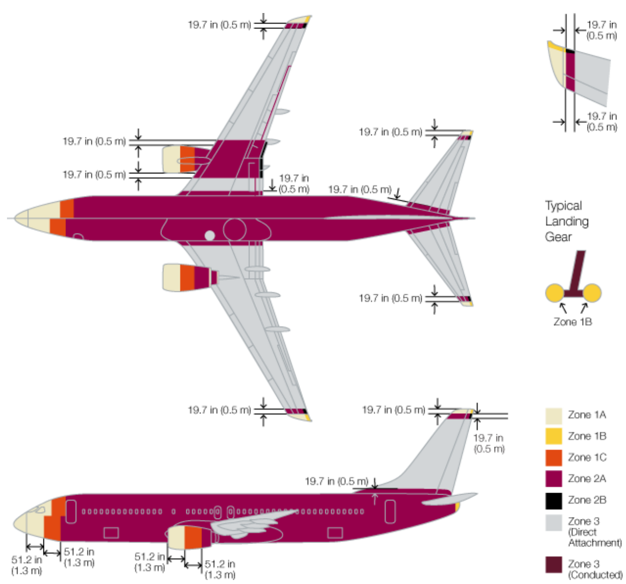


Figure 23. Aircraft Lightning Zones per SAE ARP 5414

5. CONCLUSIONS

A new BMI surfaced composite structure has been developed and exhibited excellent surfacing properties, fluid resistance and paint adhesion. Additional work is in progress to evaluate and confirm the lightning strike protection properties of the new film. With the excellent properties displayed to this point, this work demonstrates the potential for incorporating lightweight surfacing films in BMI composites for high temperature applications. Additionally, it complements the current epoxy based surfacing film portfolio and fills a need for surfacing in higher temperature applications.

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