FINAL REPORT

Near-Infrared Radiation Based Composite Repair Using Thermoplastics as Adhesives

SERDP Project WP-1581

DECEMBER 2007

Dr. Shridhar Yarlagadda
University of Delaware

Masanori Kubota
Kubota Research Associates

This document has been approved for public release.

Strategic Environmental Research and Development Program

This report was prepared under contract to the Department of Defense Strategic Environmental Research and Development Program (SERDP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

Abstract

This research project concerns the adhesive films used for composite repair in the aircraft industry by the Navy and Air Force. The adhesive films currently used for composite repair are epoxy based thermoset materials, which after curing show, amongst other, remarkable properties in peel and shear strength. However, when expired, thermosets are still very environmentally harmful, and need to be disposed through a hazardous waste protocol, which can be a long and cost full procedure. Therefore this work investigates the capability of using thermoplastic materials as adhesive films for composite repair.

The capability of using thermoplastics as adhesives for thermosets materials has been evaluated using a wide range of thermoplastics based on their adhesive strength. Amongst other, a Na^+-based ionomer S1856 and an adhesion promoter Ethylene Metacrylic Acid (EMAA) have shown high peel resistance but poor shear strength due to the high elongation of these polymers. Therefore series of Polyamide 12 (PA12) alloys have been tested some of which were doped with Na^+ ions for toughening, and other were alloyed with adhesion promoter EMAA. Another PA12 based epoxidized polymer was alloyed with Styrene Butadiene Copolymer (SBC). The results showed that a lower peel and shear resistance was achieved with a 30% EMAA promoter, while good resistance was seen with lower (15%) or no EMAA content. Little difference is seen between the 15% and the 0% EMAA PA12 alloys, for both the shear and the peel test. The influence of Na^+ toughening could not be established; as the samples showed similar values in both cases. On the other hand, The PA12-epoxidized SBC showed high peel and shear strength; 0.648 kN/m for the peel strength, and 20.6 MPa for lap shear tests. Both values are higher than the thermosets baselines (AF563M from 3M, and FM300K from Cytec), and therefore the PA12-epoxidized SBC shows great potential for structural adhesives.

Nevertheless, further studies such as hot-wet lap shear and creep testing need to be made in order to meet all the requirements. In addition further studies will be made on the influence of processing parameters such as dwell time and temperature on the adhesive properties of the thermoplastics. A study on the thickness of the film should also be made as it seems that the adhesion increases with thinner films for both lap shear and peel test.

Acknowledgements

The financial support of the U.S. Department of Defense Strategic Environmental Research & Development Program is hereby acknowledged.

Contents

1. Introduction p 3

2. Carbon fiber / epoxy pre-impregnated p 4

2.1 Material used p 5

2.2 Processing p 5

2.3 Panels characteristics p 7

3. Experimental p 9

3.1 Surface preparation repair procedure p 9

3.2 Effect of surface preparation parameters and variation in parameters p 12

3.3 Curing conditions p 14

3.4 Peel strength properties p 15

3.5 Shear strength properties p 17

3.6 Coating with thermoplastic paste p 19

4. Results and Discussion p 19

4.1 Selecting thermoplastic candidates and baseline p 20

4.2 Peel Strength p 22

4.3 Shear Strength p 29

4.4 Factors to consider p 32

4.5 Candidates with great potential p 34

5. Further studies p 35

5.1 Determining the influence of the parameters p 35

5.2 Future investigation p 36

6. Conclusions p 36

References p 38

1. Introduction

Founded in 1974 within the University of Delaware's College of Engineering, the Center for Composite Materials (CCM) is an internationally recognized, interdisciplinary center of excellence for composites research. CCM's 30,000 m^2 Composites Manufacturing Science Laboratory houses some $8 million worth of composites manufacturing, characterization, testing, and computational equipment used by students, staff, and industrial and Army interns from both the United States and abroad.

CCM, designated "center of excellence" in 1985, has developed core competencies in a number of composites science and engineering areas. These core competencies are applied to the Center's many research programs, which are supported by a variety of funding sources, including the U.S. Army Research Laboratory (ARL), the Army Research Office (ARO), the Office of Naval Research (ONR), industry (100+ companies, such as Boeing, EADS, Dassault Aviation, representing materials suppliers and end users in the aerospace, automotive, civil engineering, and durable goods industries), the Defense Advanced Research Projects Agency (DARPA), the National Academy of Science (NAS), the National Science Foundation (NSF), and the State of Delaware.

All of CCM's government and industrial partners benefit from a unique environment, which promotes team-oriented multidisciplinary research. This environment is based on a vertical integration theme that has at its foundation the facilities and expertise needed to synthesize new resins, fibers, and sizings; develop new processes; and characterize the thermo-chemical, mechanical, and durability properties of these materials from the nano- to the macro-level. CCM builds on that foundation with manufacturing and prototyping capabilities to satisfy application requirements. At the highest level, CCM has full CAD/CAM design and manufacturing capabilities to turn customers' concepts into reality using the latest materials and processing technologies. CCM's capabilities in multi-scale materials, process, and performance modeling enable accelerated insertion of materials into evolving and new applications.

CCM's current profile consists of [1]:

- More than 250 CCM-affiliated personnel
    - 45 affiliated faculty
    - 38 research professionals
    - 13 postdoctoral fellows
    - 32 Visiting scholars
    - 51 graduate and 63 undergraduate research assistants
    - 13 members in the administrative team
- More than $9 million in annual expenditures
- More than 3500 companies benefited from affiliation with CCM
- More than 2000 alumni worldwide

This project has been funded by the Strategic Environmental Research and Development Program (SERDP). It is the Department of Defense's (DoD) environmental science and technology program, planned and executed in full partnership with the Department of Energy and the Environmental Protection Agency. The aim of the SERDP is to address the highest priority issues confronting the Army, Navy, Air Force, and Marines, by pursuing high-risk/high-payoff solutions to the Department's most intractable environmental problems. The development and application of innovative environmental technologies support the long-term sustainability of DoD's training and testing ranges as well as significantly reduce current and future environmental liabilities.

This research project concerns the adhesive films used for composite repair in the aircraft industry by the Navy and Air Force. The adhesive films currently used for composite repair are epoxy based thermoset materials, which after curing show, amongst other, remarkable properties in peel and shear strength. However, as the curing reaction of these epoxy thermoset materials is also present at room temperature, adhesive films have to be stored below 0°C (usually in a freezer at -40°C). Although stored under the specified conditions, thermoset adhesives have a limited shelf life, normally about 1 year, depending on the adhesive. When expired, thermosets are still very environmentally harmful, and need to be disposed through a hazardous waste protocol, which can be a long and cost full procedure. Regarding the repair procedure, thermoset adhesives have to be cured through a specific cycle, which includes a several hours long soak time. As a whole, thermoset adhesives have intractable issues, concerning storing, processing and disposal for their use as a repair material.

This work investigates the capability of using thermoplastic materials as adhesive films for composite repair. Thermoplastics can be stored long-term at room temperature, are non-toxic and require a smaller dwell time when processed. The main objective is to find several thermoplastics, which meet the main criteria for composite repair adhesive films, from a list of pre-selected potential candidates. Thermoplastics candidates are evaluated using a standard preparation procedure from the NAVAIR, and tested using ASTM standards in order to meet the aircraft industry requirements.

2. Carbon fiber / epoxy pre-impregnated

The thermoplastic adhesive film being elaborated in this project is proposed as an alternative for thermoset adhesives, and its application is mainly intended for the aircraft industry. Therefore it has been decided, for the purpose of this project, to use a carbon fiber / epoxy based material as the structural material for testing different adhesives. It is important that the material chosen is currently being used by the aircraft industry, and shows a long-term involvement in this field, so that it can be directly correlated to present and future applications.

2.1 Material used

The material used as the substrate for the specimens in this project is a pre-impregnated unidirectional carbon fiber / epoxy material of type T800S/3900-2. It is a product of Toray Composites America, developed as a cost effective alternative to T800H, it is currently being used for the construction of the upcoming Boeing 787. T800S consist of a 350°F toughened epoxy resin, with a 60 %vol. of carbon fibers. The never twisted fiber has excellent tensile composite properties and is specifically designed to meet the weight saving demand of aircraft and high performance recreational products. Fiber properties are listed in Table 1.

Table 1
Fiber Properties[2]

	Metric	English	Test Methods
Tensile Strength	5 880 MPa	850 ksi	TY-030B-01
Tensile Modulus	294 GPa	42.7 Msi	TY-030B-01
Strain	2.0 %	2.0 %	TY-030B-01
Density	1.80 g/cm^3	0.065 lbs/in^3	TY-030B-01
Filament diameter	5 μm	$2.0 \cdot 10^{04}$ in.	

The table above only shows the properties of the carbon fibers, excluding the epoxy-based matrix. The final properties will depend on the curing cycle, and will be exposed in section 2.3.

2.2 Processing

2.2.1 Lay-up

The T800S pre-impregnated sheets come on a 0.61 m (24in.) wide roll, supported on a wax paper, to prevent undesired bonding between layers. Panels were made with a 24 ply quasi-isotropic lay-up. Two panels were made to fit the maximum size of the autoclave tray, taking into account the space required for the bagging material on the circumference. The final dimension of the two plates was 0.48 x 1.14 m (19 x 45 in.). The 24 ply quasi-isotropic lay-up was performed with the following orientation:

0°/+45°/-45°/90°/0°/+45°/-45°/90°/0°/+45°/-45°/90°//90°/-45°/+45°/0°/90°/-45°/+45°/0°/90°/-45°/+45°/0°

When cutting the prepreg (pre-impregnated) sheets in the specific orientation, it is extremely important to make sure that cuts are only performed in the longitudinal direction (in between fibers), and not perpendicular to the fibers. If fibers are sliced during the cutting process then the load will no longer be transmitted along the fiber, and failure will occur more rapidly. It is therefore essential that fibers maintain their integrity as shown in Fig. 1. After lying down each layer, cold press is performed with a hand tool (e.g.: cold iron) in order to eliminate voids, and/or folding.

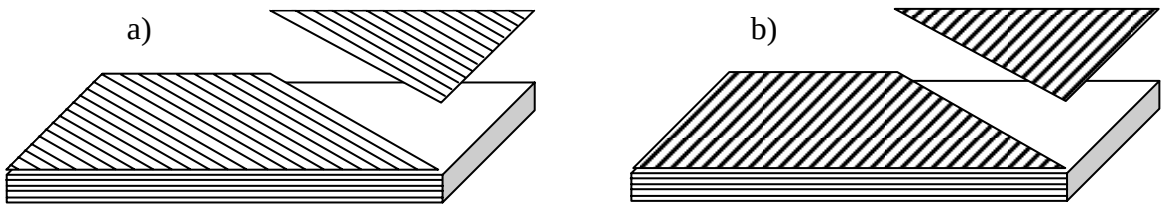


Fig. 1 a) fiber integrity is maintained, b) fiber are sliced, and no longer carry load

2.2.2 Autoclave

The curing of the prepreg composite is performed in an autoclave, as required for the aircrafts specifications. Prior to running the cycle, a specific set-up is necessary, which is commonly given by the manufacturer. The set-up used for the two panels made is shown in Fig.2. Releasing film is placed between the panel and the tray for removal purposes at the end of the curing cycle. The Peel Ply is a Teflon based fabric which is placed on both top and bottom of the composite panel, it ensure a path for the air to flow when vacuum is drawn, and gives a certain roughness to the surface finish of the panel after curing. The S-glass fibers are used as a bleeder during the curing process. During the curing cycle, pressure is applied, and there is an excess of resin, which is forced outside the panel. The glass fibers provide a path for the excess resin to flow, and is by then called a bleeder. The more layers of S-glass fibers, the more bleeding will occur. The optimal amount of bleeder required will depend on the resin content (whether the prepreg is resin rich or not) of the prepreg. However, a general rule of thumbs states that for every 4 plies of prepreg material, 1 layer of s-glass fiber is needed. In our case, T800S has a 60 %vol. fiber content, and the general rule was applied. Finally a bagging film is used in order to seal the content, using black tacky tape on the circumference. The vacuum line is within the airtight area and ensures a pressure of approximately 0.96 bar (14 psi).

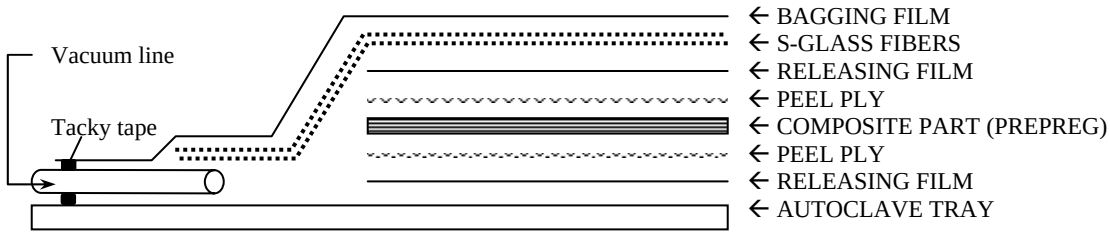


Fig. 2 General set-up for curing prepreg in the autoclave

The autoclave used for this experiment is a 1990 model manufactured by Thermal Equipments Corporation (TEC) (Fig. 3). It can reach a maximum pressure of 35 bar (515psi), a maximum temperature of 540°C (1000°F), and contains a volume of 0.34 m^3 (12.5 ft^2).

The curing cycle for a thermoset is of great importance, for the final mechanical properties. The temperature and dwell time determine the amount of cross-linking during the curing cycle, which affects the toughness of the material. If an extensive dwell time, or an excessive temperature is used, a destructive reaction will be initiated, and the thermoset will start to degrade. Commonly, the exact curing cycle is given by the manufacturer for optimal mechanical properties.

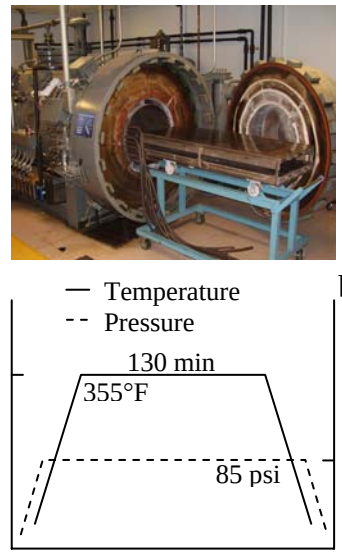


Fig. 3 a) Autoclave, b) curing cycle

The sample has to be bagged under vacuum pressure 0.96 bar (14 psi), and a pressure of 5.86 bar (85psi) has to be applied throughout the curing cycle. It is recommended to first start the cycle by pressurizing the autoclave to 1.38 bar (20psi) and vent the bag to atmosphere, because once the pressure is above 0.96 bar, the vacuum is no longer necessary. Only then increase the pressure to 5.86 bar (85psi). The laminate should be heated up to a temperature of 180°C ±5°C (355°F ±10°F) at a rate of 0.5 to 2.5°C/min (1 to 5°F/min). The dwell time at 180°C ±5°C (355°F ±10°F) is 130 ±10 minutes. After dwell the temperature of the autoclave should be decreased at a temperature not to exceed -2.5°C/min (-5°F/min). Only when the laminate reaches a temperature of 60°C (140°F), the autoclave pressure may be reduced to ambient.

2.3 Panels characteristics

After curing, the panel thickness is slightly smaller around the edges. The main reason is due to the fact that the plies are not being added perfectly on top of each other. Another reason is that there is a higher amount of bleeding around the edges and corners of the panels. For that reason, the outer most 0.5 inches of the panels are trimmed off. The panels' thickness is measured after curing, and the average value measured is 4.20mm (0.165in.) for our 24 plies panels. In other words we have a post-cured thickness per ply of 0.175mm (0.0068in.). This calculation is a good approximation in order to find the number of plies required to reach a specific panel thickness.

As mentioned in the autoclave lay-up, the surface of our panels has a peel ply finished surface. Therefore our final surface has a certain roughness defined by the impregnation of the peel ply on the panel. The surface topography has been examined using a Scanning Electronic Microscope (SEM), model JSM-7400F. For the analysis of our samples, a field emission tip, and a voltage of 3 keV were used for the electron source. Fig. 4 shows the SEM image of a) the T800S panel with a peel ply surface finish, and b) a surface ground with 180 grit sand paper. In the first case, the element analysis showed a relative percentage of 84.5 %at. C, and 15.5 %at. O at the surface. On the other hand, the ground surface with 180 grit sandpaper, showed 89.8 %at. C, and 10.2 %at. O at the surface. The results are very similar and coherent, the increase in carbon content for the second case is simply due to the grinding process, which removes a majority of the matrix at the surface, but doesn't damage significantly the carbon fibers. Therefore less oxygen from the epoxy group is present at the surface.

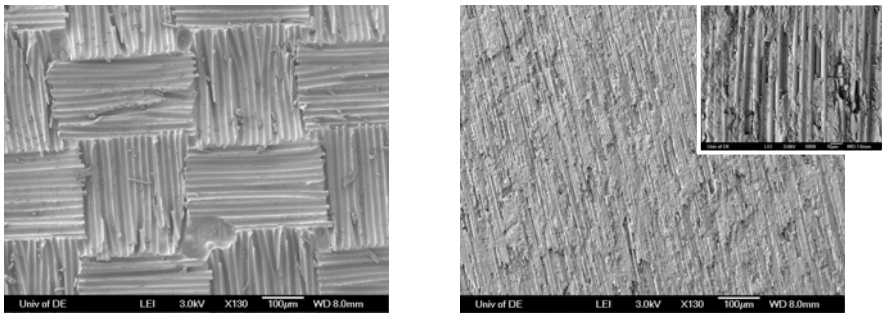


Fig. 4 a) the T800S panel with a peel ply surface finish, and b) a surface ground with 180 grit sand paper

On the peel ply surface finish; the carbon fibers are not visible, as they are recovered by a layer of the epoxy resin, which has adopted the shape of the peel ply. On the other hand, on the ground surface, the carbon fibers are visible. At greater magnification, we can see that the 5 µm fibers are intact, and are not damaged by the grinding process. The surface preparation procedure will be described in section 3.1.

Furthermore, intent has been made to measure a value of the roughness of the ground surface. This was done through AFM (Atomic Force Microscopy) using a Zygo machine. The surface topography is shown in Fig. 5. Measurements of the surface roughness were made in both x and y directions. When measuring on the longitudinal axis (along the fiber direction), the roughness was around 5µm. However, on the perpendicular axis, the roughness was approximately 10µm.

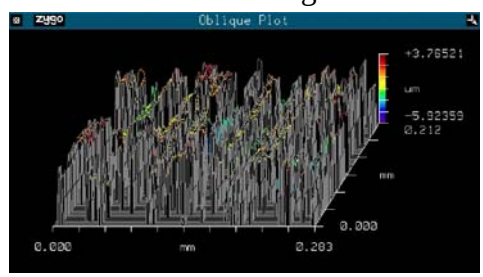


Fig. 5 AFM Surface roughness

The common properties of the panels after curing are shown in Table 2. This data is obtained from the Toray T800S Technical Data Sheet No. CFA-019 and should represent the properties of the panels cured with the specified T800S curing cycle. The T800S composite materials shows a good tensile and compressive strength at room temperature, and shows little influence of temperature on these properties, at both -60°C and 82°C.

Table 2. T800S Properties [2]

	Metric	English
Tensile Strength (Room Temp.)	2 950 MPa	430 ksi
Tensile Strength (-60°C/-75°F)	2 860 MPa	415 ksi
Tensile Modulus	154 GPa	22.5 Msi
Open Hole Tensile Strength	487 MPa	70.5 ksi
Open Hole Compressive Strength (Room Temp.)	291 MPa	42.0 ksi
Open Hole Compressive Strength (82°C/180°F/wet)	229 MPa	33.0 ksi

3. Experimental

The accuracy of the results of strength tests of adhesive bonds will depend on the conditions under which the bonding process is carried out. Therefore it is essential to use bonding procedure, which meet the specifications required by the aircraft industry. Furthermore the testing standards used should be in accordance with the standards used bye the aircraft industry, in order to make direct comparison of the results. The experimental procedure developed in this project has been established in the intention to respond as much as possible to the aircraft industry requirements.

3.1 Surface preparation repair procedure

When it comes to testing the adhesive strength of structural adhesive films, the procedure used for surface preparation is the most important and critical step. Eventually if the surface preparation procedure is not appropriate or not followed correctly, the tests results will not be coherent and direct comparison between samples will be impossible. The surface preparation procedure for this project has been taken directly from the NAVAIR Technical Manual on General Composite Repair, NAVAIR 01-1A-21. The procedure followed from the manual concerns penetration damage and implies bonded repair. This repair is applicable when an externally bonded patch is required. This includes partial thickness damage, penetration damage, unsuccessful disbands injections and damage involving honeycomb core.

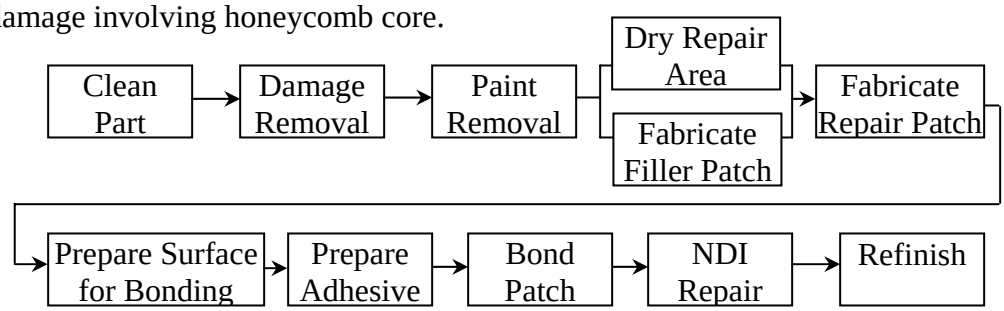


Fig. 6 Process Flow Diagram for Penetration Bonded Repair[3]

3.1.1 Clean Part

- Mask all penetrations and openings using water-vaporproof barrier material[1] and pressure sensitive tape[2] to avoid water intrusion and resultant part damage during the cure process of a bonded repair.
- Detergent clean the part using cleaning compound[3]. Apply cleaner solution to the part using rymplecloth[4].
- Scrub the solution into stubborn areas using a non-metallic bristle brush until the surface deposits are loosened.
- Rinse part with fresh water and dry with clean dry rymplecloth.

1 Water-Vaporproof Barrier Material, MIL-B-131, Class II
2 Pressure Sensitive Tape, MIL-T-23397, Type II
3 Cleaning Compound, MIL-C-85570, Type II
4 Rymplecloth, MIL-C-87962, Type I

3.1.2 Damage Removal

- Determine the damage extent using Non Destructive Inspection (NDI).
- Remove NDI couplant by wiping with clean, water moistened rymplecloth.
- The cutout radius shall not be less than 0.5 inch.

3.1.3 Paint Removal

- Apply masking tape[1] to mask off the repair area and to provide a paint removal boundary.
- Remove paint by sanding by hand or with an orbital sander. Use 80-120 grit abrasive paper initially.
- When primer is visually detected on the part, change to 180-240 grit abrasive paper.
- Wipe area with clean, dry rymplecloth to remove remaining sanding residue.

3.1.4 Dry Repair Area

- Layup the heat blanket, thermocouples and vacuum bag.
- Specified drying temperature 210 ±10°F.
- Apply 20-30 inches of mercury vacuum to the vacuum bag. Heat the repair area to the specified temperature at a rate of 2-6°F per minute.
- Hold specified temperature for 2 hours and maintain 20-30 inches of mercury vacuum.
- Cool to room temperature at a rate not to exceed 5°F per minute.

3.1.5 Fabricate Filler Patch

- If applicable, fabricate a filler patch from carbon/epoxy patch material. Multiple layers of patch material may be used to meet thickness requirements.

3.1.6 Prepare Surface for Bonding

The simplicity and high degrees of bond durability of this process has contributed significantly to the reparability of advanced composite parts. Unlike metallic parts, the surface preparation does not require an elaborate and process sensitive procedure using chemicals that are difficult to work with and dispose of to obtain a successful bond.

CAUTION:

Do not use solvent to remove sanding residue. The solvent can spread a thin film of contamination over the entire bond surface if it is not wiped off before it evaporates. Since the solvent evaporates quickly, it usually evaporates before the surface can be wiped dry.

1) The Surface preparation for resin matrix composites consists of sanding with 180 grit abrasive paper and repeated dry wiping with clean dry rymplecloth until no further evidence of sanding residue appears on the cloth.

a) Use rymplecloth[1] for wiping instead of cheesecloth. Rymplecloth is a purified cheesecloth that has been bleached to remove cotton seed oil and fiber sizing. This will reduce the potential for contamination of surfaces to be bonded.

---

1 Masking Tape, A-A-883, Type I

1 Rymplecloth, MIL-C-87962, Type I

b) Cover surfaces prepared for bonding with clean barrier material[2] to prevent contamination while preparing for lay-up.

2) The Patch surface.

NOTE:

If the patch is procured and contains peel ply material, the peel ply should be left on the patch until the surface preparation step, to prevent contamination.

a) Cautiously remove the peel ply from both surfaces of the patch to prevent pulling fibers out of the patch material. If fiber removal starts during peel ply removal, change the peel ply removal direction so that peel ply is being removed 90 degrees to the patch outer ply fibers.

b) If the patch is cut from procured carbon/epoxy square sheet stock, the edge of the patch must be tapered. This taper is required to reduce adhesive peel stresses at the edge of the patch. First cut the patch from procured carbon/epoxy square sheet stock to the dimensions required for the repair patch. Then, taper the patch edge as shown in Fig. 7. Use a 90 degree router motor and an 80-100 grit abrasive disk.

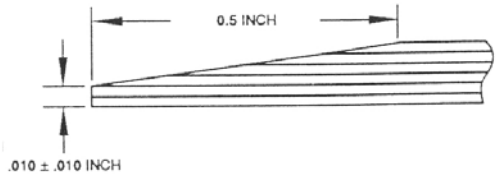


Fig. 7 Patch Edge Taper Dimensions[4]

c) Sand by hand (or with an orbital sander) both surfaces of the patch with 150-180 grit abrasive paper. Ensure that the majority of any peel ply impressions on the patch surface are removed as these impressions can act as recesses that will trap air and other vapors. Sand carefully to minimize removal of load carrying fibers. Ensure 100% coverage of the patch surfaces during sanding.

d) The patch still requires sanding even if peel ply was not used during patch manufacture (peel ply impression will not be present on patch surface). This will remove any potential contamination from the patch manufacturing process and will roughen the surface ensuring a high quality, durable bond.

e) Wipe the sanded surfaces with a clean, dry rymplecloth to remove sanding residue. Inspect the cloth for evidence of sanding residue. Repeat wiping process until no evidence of sanding residue exists on the cloth. For each repeat wipe use a new, clean, dry rymplecloth.

f) From this point forward, handle the patch wearing clean white cotton gloves[1]. Cover the patch with clean barrier material until ready for lay-up.

---

2 Barrier Material, MIL-B-121, Type II, Grade A, Class I

1 White Cotton Gloves, 8415-00-268-8353

3.1.7 Prepare Adhesive

- Remove adhesive from 0°F storage, and allow reaching room temperature (approximately two hours). Material exposed to temperatures above 0°F for more than 24 hours must be considered suspect, and should be tested as describes in paragraph 5-6a before using.
- Cut a piece of film adhesive ¼ inch larger than the patch bond area.
- Remove all separator plies from adhesive.
- Repeat wipe of bond surfaces with clean dry rymplecloth.

NOTE:
FM300 film adhesive are embossed with a honeycomb core imprint on one side.
Apply the embossed side to the part surface.

3.1.8 Bond Patch

- Center adhesive and patch over repair area and tape into position.
- Repeat steps for next patch, in a multi-patch lay-up. Tape in place with high-temperature tape.

3.1.9 NDI Repair

- Visually inspect adhesive squeeze out at patch edge.
- Perform NDI of patch to skin and patch to filler bond areas to verify bond line integrity.

3.1.10 Refinish

- Sand the area smooth with 180 grit abrasive sand paper.
- Apply finish system.

3.2 Effect of surface preparation parameters and variation in parameters

3.2.1 Variation in the extent of grinding

Fig. 8 Surface grinding

An eccentric palm grinder was used for surface grinding with 180 grit sand paper, in order to keep the amount of grinding constant throughout the samples and consequently obtain more coherent results. However the extent to which grinding is performed on the composite materials will influence the total surface area, and consequently the adhesion strength. For this reason 2 different samples have been tested using a thermoset baseline adhesive film (FM300K), and with different grinding times. A first sample, labeled “light grinding” has been lightly ground with passing the palm grinder only 5 to 6 times over the sample, therefore removing most of the peel ply impression. The second sample labeled “heavy grinding” has been ground until all the peel ply impressions disappeared, leaving a nice and shiny surface. The rest of the procedure was constant and the curing cycle was performed simultaneously with the same baseline adhesive film. A peel test was performed on the samples, and showed the results displayed on Fig. 9. The results show that there is little influence of grinding on peel strength, however there is still a slight preference for the light grinding due to the larger surface area available for bonding.

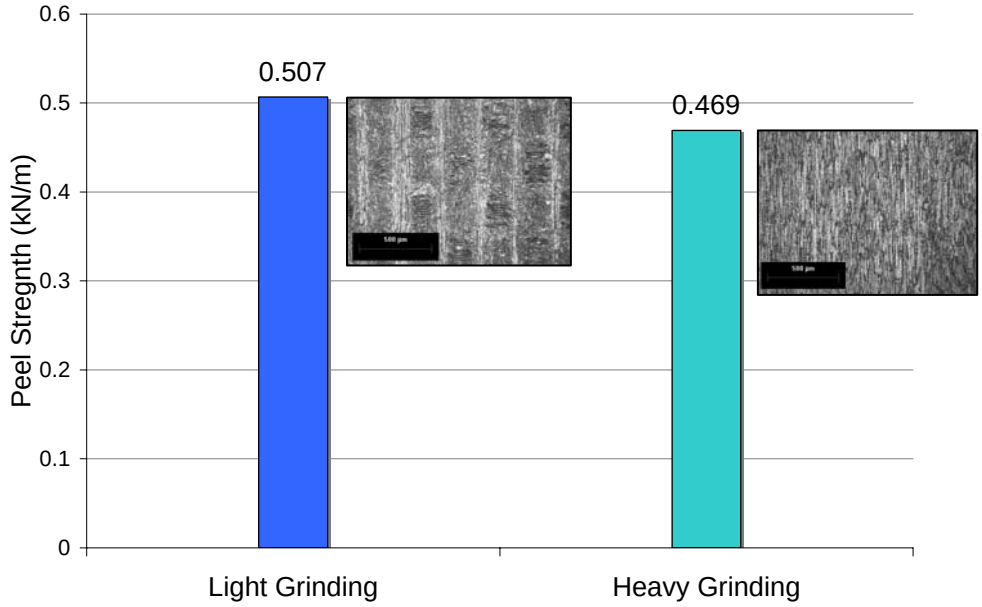


Fig. 9 Influence of the extent of grinding on peel strength

3.2.2 Effect of surface preparation

Surface preparation was therefore performed with the amount of grinding defined as "light grinding". Nevertheless, there is a great influence on the surface preparation method selected for adhesive bonding. In fact, the NAVAIR has been compared with another general surface preparation method, which consists in sand blasting, followed by acetone cleaning to remove the residues. The results shown in Fig.10 have been obtained using the FM 300K Adhesive film. The NAVAIR procedure provides a peel strength more than 1.5 times bigger than the usual procedure. This example is a good illustration of the importance of surface preparation for bonding.

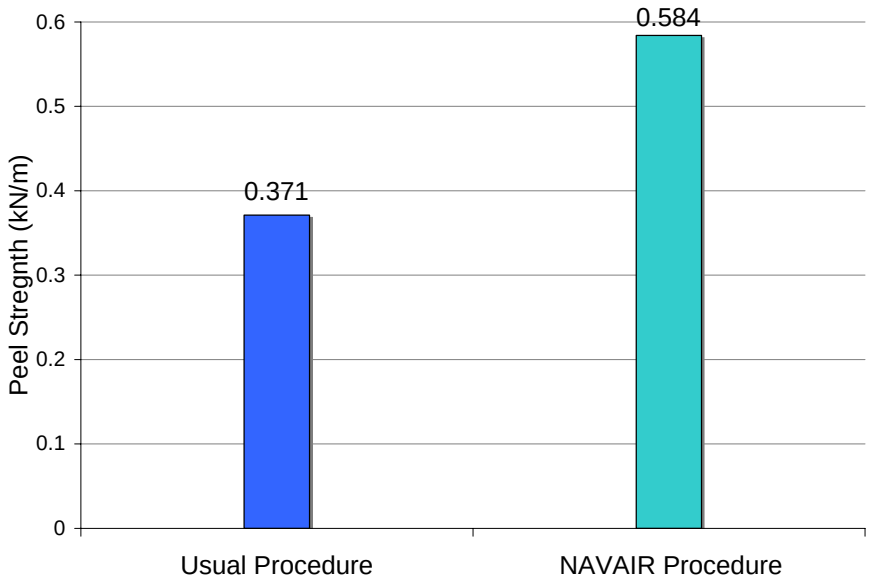


Fig. 10 Influence of surface preparation on peel strength

3.3 Curing conditions

The curing cycle for the thermosets was given by the manufacturer. 2 Thermosets adhesives were used as a baseline. FM 300K manufactured by Cytec Engineered Materials, and the AF563 manufactured by 3M. Both are used in the aircraft industry as structural adhesives. In both cases the curing cycle given by the respective manufacturer was followed. However for the FM 300K a different curing cycle (recommended for repair procedure) was used, which consisted of a lower temperature and a longer soak time, when compared to the default cycle.

Kubota Research Associates manufactured all the thermoplastics candidates, and recommended a temperature cycle for each one of them. The temperature cycle for thermoplastics requires a shorter soak time, because there is no reaction involved, and the only concern is to use a sufficiently long soak time, to ensure homogeneity of the temperature profile across the film when the polymer is at melt. Once the temperature is considered homogenous, the sample can be cooled. It is important to understand that at the end of the soak time, thermoplastics are liquid, and only start to solidify as the temperature is decreased. In fact during the solidification of thermoplastics, and for crystalline or semi-crystalline polymers only, crystals will begin to form and grow until the polymer is completely solidified. The birth and growth of the crystals strictly depend on the cooling rate. A slower cooling rate will allow crystals to grow bigger, while a faster cooling rate will results in little and small crystals. In the end, the properties of the thermoplastic will depend on the portion of crystalline and amorphous phase present in the polymer. Therefore the most important part of a temperature cycle for a thermoplastic is the cooling, as it defines the final properties of the polymer.

On the other hand, the temperature cycle for thermoset needs to take into account the curing reaction, which is taking place during heating. Enough time has to be given to ensure a maximized cross-linking of the resin during the curing phase. In other words, the curing process is a chemical reaction, which generates cross-linking between molecules, and therefore the thermoset solidifies as the cross-linking increases. Hence, at the end of the soak time, the thermoset is solidified. The cooling phase stops the ongoing chemical reactions, and its rate is not critical.

In addition to thermoset and thermoplastic films being tested, a “Parent Material Durability” has been evaluated by curing the two pre-impregnated parts together without any adhesive film in between. The same curing cycle as the fabrication of the panels was completed in the autoclave. The “Parent Material Durability” sample will reveal information about the adhesive strength within the composite material itself. In other words it will evaluate the force required for failure between the carbon fiber and the epoxy resin and/or the cohesive failure of the epoxy resin itself. Table 3 summarizes the temperature cycle for different samples.

Table 3 Temperature cycle for different adhesive films

Sample	Soak Temperature	Dwell Time min	Cooling rate °C/min	Pressure
Parent Material Durability				
T800S/3900-2	180°C (355°F)	130	-	85 psi
Thermoset Baseline				
AF 563M	135°C (275°F)	90	-	Vacuum
FM 300K	152°C (305°F)	240	-	Vacuum
Thermoplastic Films				
Ionomer S1856	175°C (347°F)	60	1.2	Vacuum
EMAA N1207C	175°C (347°F)	60	1.2	Vacuum
PA12 Alloy	180°C (355°F)	60	1.2	Vacuum
PA12 Epoxidized SBC	185°C (365°F)	60	1.2	Vacuum
PA12 N0	185°C (365°F)	60	1.2	Vacuum
PA1285 N15	185°C (365°F)	60	1.2	Vacuum
PA1270 N30	185°C (365°F)	60	1.2	Vacuum
PA1285 S15	185°C (365°F)	60	1.2	Vacuum
PA1270 S30	185°C (365°F)	60	1.2	Vacuum
PA6 Alloy	230°C (446°F)	10	-	Vacuum
Thermoplastic Paste				
PA6 CPA	230°C (446°F)	10	-	Vacuum

(Vacuum): 0.96 bar (14 psi)
(-): Not recorded

3.4 Peel strength properties

In order to test the peel strength of adhesives, a standard test method from the ASTM was used. The Floating Roller Peel Resistance of Adhesives ASTM D 3167 – 03a (2004) is a method that will provide good reproducibility at low, as well as at high strength levels and yet allow for a simple method of test specimen preparation and testing. It allows determining the relative peel resistance of bonded adherends, where one adherend is made to be rigid and the other adherend is made to be flexible.

3.4.1 Sample Preparation

The rigid adherend was cut from the panels, which elaboration is described in section 2.2, with dimensions of 76.2 x 203.2 mm (3x8 in). The flexible adherend was made from a single ply of the same material (T800S/3900-2) and with the same curing cycle. The dimensions of the flexible adherend are 76.2 x 254 mm (3x10 in). Both adherends have been submitted to the NAVAIR surface preparation requirements, and put together as displayed on Fig. 11. The bonded panels were cut into 12.7 mm (0.5 in) wide test specimens.

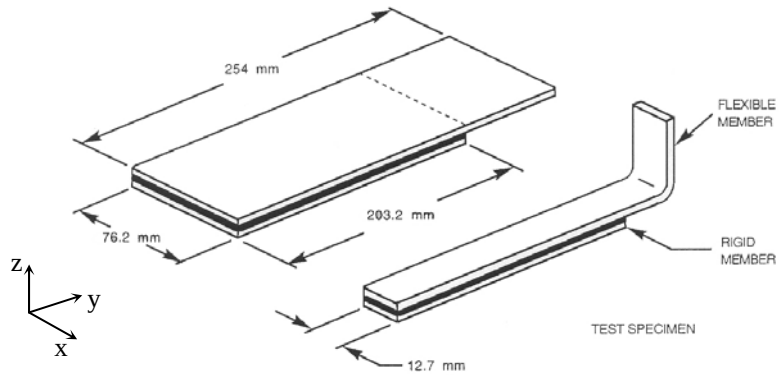


Fig. 11 Test Panel and Test Specimen

The test panels need to be cut by means that is not deleterious to the bond, for this reason a slot grinder was used. The slot grinder was used with a diamond coated blade, with back and forth movement in the y direction. For each cycle, the blade would increment by 0.01in in the negative z direction. The small progressive increment guarantees that no damage is done to the bond. In addition, when cutting the test panels, the direction of the carbon fiber was taken into consideration. For instance, the flexible adherend were cut so that the fibers are oriented in the longitudinal (y) direction. On the other hand, the rigid adherend is cut so that the fibers of the outer most ply are oriented in the x direction. It is very important that this orientation is kept constant for all the samples.

3.4.2 Test Method

The test specimens were inserted into the peel test fixture as shown in Fig. 12, with the unbonded end of the flexible adherend gripped in the test machine jaw by at least 25.4 mm (1 in). The specimen is peeled at 152 mm/min (6 in/min) bond separation rate by applying the load at constant head speed of 152 mm/min. It is necessary that the rigid adherend is stiff enough so that it doesn't bend and is not distorted during the test, in order to ensure even peel. Furthermore, direct comparison of different adhesives may be made only when the angle of peel is identical. Therefore it is very important that the flexible adherend is bending over the mandrel and not at some irregular angle. For this reason the flexible adherend cannot be thicker than a single ply of carbon fiber prepreg. During the test an autographic recording of load versus head movement (load versus distance peeled) is made.

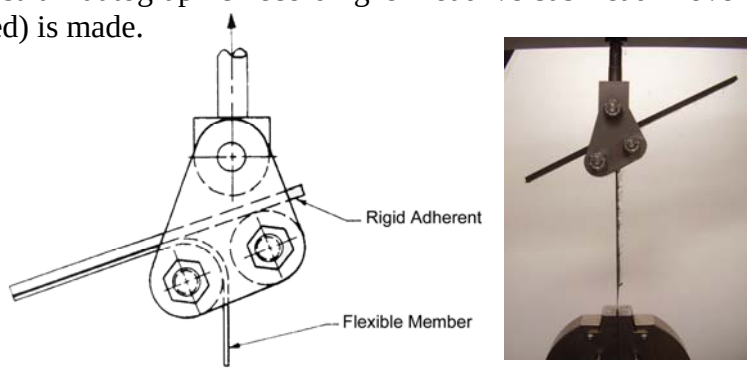


Fig. 12 Roller Drum Peel Test Fixture

3.4.3 Calculations

From the autographic curve, the average peeling strength is calculated in kN/m disregarding the first 50 mm of peeling, and over 100 mm. So the average value is calculated from the load recorded from 50 to 100mm of the peeling only. The average load in kN is divided by the width of the sample (length over which the force is applied) in m. For every set of 6 specimens, the mean of the peel strength is calculated, along with the standard deviation. Samples are considered outlier when the average peel strength lies outside the range of $\pm 1.75\sigma$ (where σ is the standard deviation).

3.5 Shear strength properties

The major failure type of adhesive films is a combination of both peel and shear forces. Therefore it is necessary to study the resistance to both types of failure if we wish to look at its behavior for this application. The standard method used in this section corresponds to the standard for most aircraft applications, and is used by Cytec Engineered Materials to compare properties of thermosets adhesive films. The method is the Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Specimens by Tension Loading ASTM D 1002 – 05.

3.5.1 Sample Preparation

Panels of 101.6 x 177.8 mm (4x7 in) were cut from the T800S panel made in the autoclave. Two 101.6 x 177.8 mm panels are superposed with 25.4 mm (1 in) overlap, where the adhesive is applied (Fig. 12). Since it is undesirable to exceed the yield point of the composite samples in tension during test, the permissible length of overlap in the specimen varies with the thickness and type of material used and the general level of strength of the adhesive being investigated. The overlap distance used for the carbon fiber / epoxy material was 25.4 mm (1 in). However the maximum permissible length may be computed from the following relationship:

$$L = Fty \cdot t / \tau$$

where:

L = length of overlap, in.
t = thickness of specimen, in.
Fty = yield point of material (or stress at proportional limit), psi.
τ = 150 % of the estimated average shear strength in adhesive bond, psi.

The surface of the panel is treated as required by the NAVAIR surface preparation procedure. A stripe of 2.54 x 177.8 mm (1x7 in) of the adhesive film is cut and placed in the overlap area between the two panels. The adhesive is then cured to the panels in the oven, following the respective curing cycle of the manufacturer. After the curing process, 25.4 mm (1 in) wide specimens are cut from the panel as shown in Fig. 13. The specimens were cut, with the slot grinder, so that the fibers of the outer most ply are oriented perpendicular the axis of load. This way there is a greater chance for mechanical interlocking between the bonded surfaces, and therefore a higher shear strength will result.

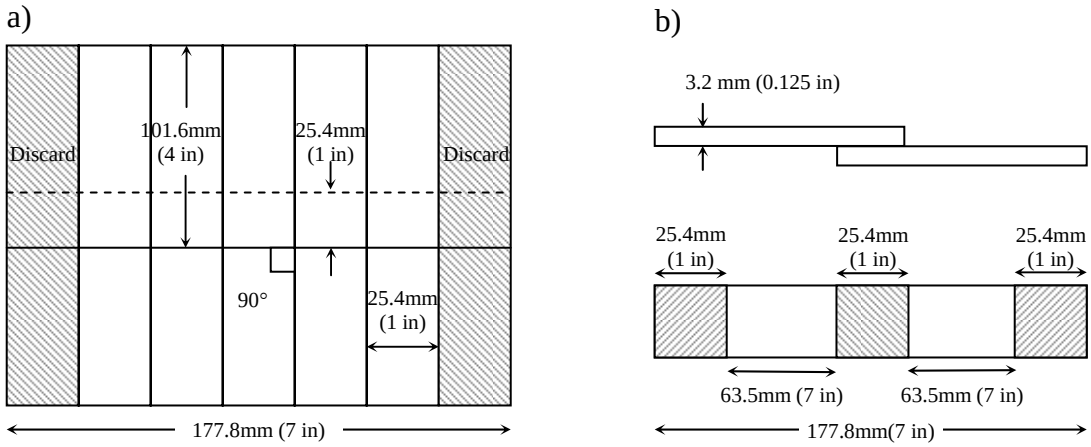


Fig. 13 a) Standard Test Panel and b) Specimen for Shear testing

3.5.2 Test Method

The specimen is placed in the grips of the testing machine so that the outer 25 mm (1 in) of each end are in contact with the jaws. Spacers of the same material and thickness as the sample are used to compensate the fact that the two ends of the specimen are not aligned (see Fig. 14). By using a spacer of the same material and the same thickness, we ensure that the specimen is aligned and that there is no torque acting on the specimen. Nevertheless it is necessary to be very precautious when tightening the grips, in order to make sure that no torsion is applied, which could facilitate the failure of the specimen during the test. The load needs to be applied at a rate of 80 to 100 kg/cm^2 of the shear area per min. This rate of loading is approximated by a free crosshead speed of 1.3 mm (0.05 in)/min. The load is continued until failure. During the test an autographic recording of load versus head movement is made.

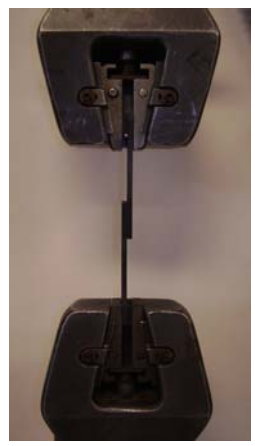


Fig. 14 Shear Test

3.5.3 Calculations

For each run, the maximum, minimum, and average values for the failing load are calculated, and divided by the surface area of overlap used, in order to obtain the shear strength in MPa. Furthermore the nature of the failure is established, and prior to testing the thickness of the adhesive layer is measured using a light microscope. For both peel and shear samples, an average from 6 measurements is calculated in order to estimate the film thickness. The Optical microscope image is shown on Fig. 15.

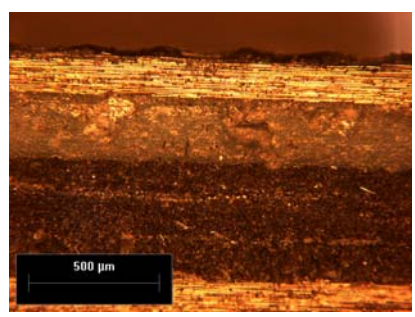


Fig. 15 Film thickness of a peel test specimen.

3.6 Coating with thermoplastic paste

As listed in Table 3, one of the thermoplastics used comes in the form of a paste, it is therefore necessary to apply the paste on the adherend by maintaining the thickness as constant as possible. This is done using a coater (Fig. 16) from Kubota Research Associates. The coating is performed on the single ply lying on a flat glass surface. The first 50.8mm (2 in) are covered with masking tape, and the paste is poured onto the single ply. At this point, the viscosity of the paste can be adjusted for optimal spread, using isopropyl alcohol. Then the surface is swiped with a metallic rod on which a filament is winded and allows for a specific thickness to be spread on the surface. The rod used allowed for a spreading thickness of 188 μm (0.0074 in). The spread thermoplastic was let to dry overnight, in order to eliminate the solvent, which is present in the paste.

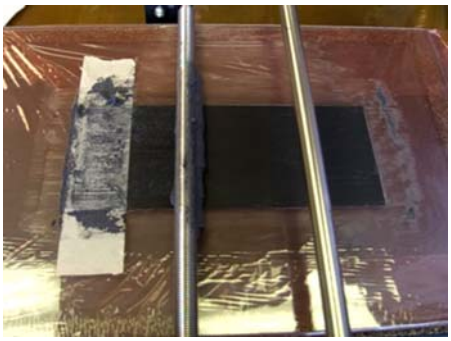


Fig. 16 Metal rod coater (188μm)

4. Results and Discussion

A structural adhesive must have strength enough to transfer or share loads between highly stressed components. A general rule of thumb is that a force of at least 6.9 MPa (1000psi) should be required to separate a bonded joint in a lap shear coupon test[5]. The structural adhesive's strength comes from a combination of different phenomena. First the adhesive's surface energy (that is, the energy inherent in the disrupted chemical bonds that occur when the surface was created) should closely match that of the substrates. If it doesn't, the adhesive will be repelled. Second, abrasion increases the adherend's surface area, which augments adhesion as the adhesive flows into and around microscopic crevices in the abraded surface, forming an actual mechanical interlock. Third, and especially for composite-to-composite bonds, the adhesive dissolves some of the adherend's polymer molecules, alloying molecules in the adhesive to form covalent chemical bonds with molecules on the adherend, helping to chemically lock the two together.

Despite advances, formulation is still a challenge. For example, tougheners added to improve elongation and impact resistance can reduce adhesive strength and glass transition temperature (T_g). Currently, three basic thermosetting resin chemistries dominate the structural adhesives market: epoxy, polyurethane and acrylic[5]. In transportation, marine and industrial applications, all three types are in common use. While in the Aerospace sector, epoxy dominates, due mainly to very high strength and temperature resistance and compatibility with the sector's predominately epoxy-based laminates such as the T800S used in this project.

4.1 Selecting thermoplastic candidates and baseline

As mentioned earlier, two epoxy-based thermosets adhesives were used as a baseline for comparison purposes. The first adhesive used is the FM300K from Cytec Engineered Materials. It is a modified epoxy adhesive and is used in most aircraft applications because it has a high elongation and toughness with high ultimate shear strength. There are two different weights for the FM300K, the one used for this project is the 244 g/m^2 (0.05 psf). It is reinforced by a thin wide open knit (K), made out of polyester fabric. The knit makes it easier to handle by avoiding stretching, keeps a constant film bondline, and allows gas to escape. It has a nominal thickness of 200 μm and the color of the film is green. The second thermoset structural adhesive film used is the AF563M manufactured by 3M™ Scotch-Weld™. It is reinforced by a lightweight matte (M) and has a density of 294 g/m^2 (0.06 psf). Its nominal thickness is 254 μm and has a red color. There are less than 0.5% of volatiles. The % flow at 121°C (250°F) cure for 60 min at 45psi is 300-360 %.

When selecting the thermoplastics candidates our first criteria is that the processing temperature stays below 180°C (355°F), as chemical degradation might occur if we exceed the curing temperature of the T800S. Furthermore a sufficient % melt flow is required during the melting process, to ensure optimal penetration of the adhesive into the microscopic crevices of the adherend. The last selective criterion is given by the service temperature, which will actually depends on which part of the aircraft the adhesive is used, or for which applications. From a list of candidates shown in Table 4, several thermoplastics have been selected for testing. Both Poly Ethylene Terephtalate (PET) and Polystyrene (PS) show too high process temperature (around 240°C for PS) for their application with epoxy-based composite materials. Ionomer commonly offer good bonding properties, but their low melting temperature limits their application. On the other hand Polyamide (PA) shows good potential for adhesion due to the high hydrogen bonding capability, especially for PA 6,6. However the melting point for PA 6,6 (285°C / 545 °F) limits its application. Thus when looking at other types of Polyamides, PA 6 and PA 12, offer lower melting temperatures, 175 ± 5°C for PA 12, and 210-230°C for PA 6. Therefore a PA 12 or a PA 12 Alloy could show some good potential.

Table 4 List of potential thermoplastics candidates and relative comparison of properties

	Melting Temperature	Melt Flow	Service Temperature	Oil and Chemical Resistance
Polyethylene Terephthalate	too high[1]	good	sufficient	sufficient
Co-Polyester	sufficient	good	sufficient	sufficient
Polyamide 6, 6	too high[1]	poor	high	good
Polyamide 6	high	sufficient	high	good
Co-Polyamide	sufficient	good	low	good
Polyamide Alloy	sufficient	good	sufficient	good
Ionomer	low	sufficient	low	good
Polystyrene	too high[1]	sufficient	sufficient	poor

1 too high for applications with epoxy-based composite materials

Finally a list of 11 thermoplastics has been chosen for testing. The first thermoplastic to consider is the Ionomer S1856 with sodium ions present in the functional group. The charged metals ions promote adhesion by creating dipole-dipole attractions, and therefore show good potential for adhesive strength. Another thermoplastic that needs to be investigated is the Ethylene Metacryclic Acid (EMAA), which is usually used as an adhesion promoter. It promotes adhesion by creating bonds between the adhesive used, and the epoxy matrix as well as the tougheners present in the matrix (which are commonly thermoplastics). Therefore the EMAA will be investigated on its own, as a pure adhesive but also as part of polymer alloy. Then, as listed in Table 5, both PA 6 and PA 12 alloys will be tested. Although PA 6 has a high melting point, if it shows good adhesive properties, it might be used for other applications were the adhesive could be processed at higher temperatures. Then, a series of five PA12 alloys is tested, on the PA12 alloy structure. The five PA12 for this series have been manufactured by hot pressing in our laboratories, as opposed to blow molding, which has been used for most of the thermoplastics described above. The first of five is a plain PA12 alloy, with no promoter. Within the other four samples, two have been mixed with 15% EMAA (adhesion promoter), and two with 30% EMAA. Then one of each composition has been doped with Na^+ ions, which is used as a toughener in order to compensate the fact that EMAA promoter usually has high elongation properties, and this could reduce the shear strength considerably.

Table 5 List of thermoplastics used for testing, and brief description

	Melting Temp. ± 5 °C	Thickness (μm) ± 20 um	Description
Ionomer S1856	86°C	50	Na associated Ionomer
EMAA N1207C	< 100°C (212°F)	50	Ethylene Metacrylic Acid (adhesion promoter)
PA 12 Alloy	175°C (347°F)	30	Polyamide 12 Alloy
PA12-Epoxidized SBC	175°C (347°F)	220	PA 12, Epoxidized Styrene Butadiene Copolymer
PA12 N0	175°C (347°F)	270	Polyamide 12 Alloy
PA1285 N15	175°C (347°F)	270	85% Polyamide 12, 15% EMAA
PA1270 N30	175°C (347°F)	290	70% Polyamide 12, 30% EMAA
PA1285 S15	175°C (347°F)	250	85% Polyamide 12, 15% EMAA Na doped
PA1270 S30	175°C (347°F)	280	70% Polyamide 12, 30% EMAA Na doped
PA 6 Alloy	230°C (446°F)	80	Polyamide 6 Alloy
PA6-CPA (Paste)	225°C (437°F)	188	Polyamide 6 and Copolyamide Paste

Another way in which the PA12 has been modified to improve its adhesion is by adding an epoxidized Styrene Butadiene Copolymer (SBC). The epoxy group is compatible with the epoxy resin from the substrate, and creates covalent bonding between the epoxy resin, and the adhesive film. At last, the thermoplastic paste is made of PA6 and copolyamide particle (approx. 40µm diameter) in a solution of isopropyl alcohol and water. The copolyamide is intended to reduce the melting temperature while maintaining the good hydrogen bonding capabilities.

4.2 Peel Strength

4.2.1 Baseline and parent material durability results

The results for both of the baselines (FM300K and AF563M) showed coherent results and a good reproducibility. As expected, the peeling load is constant across the whole length of the specimen (see Fig. 17 (AF563)). The average peeling load is taken for each sample from 50mm to 150 mm of extension, in order to discard the beginning and the end of the peeling load. The initial peek is not characteristic of the material, or the adhesive itself. It actually corresponds to the beginning of the experiment, where the rigid adherent is placed on the mandrel. The height of the peek depends on where the rigid adherend hits the mandrel in the first place. In other words, the height of the peek can be controlled by placing the adherend higher or lower in its first contact with the mandrel, and therefore should not be considered as a characteristic of the material. In each case the average peel load is divided by the width of the sample (12.7 mm / 0.5 in) in order to obtain the peel strength in kN/m.

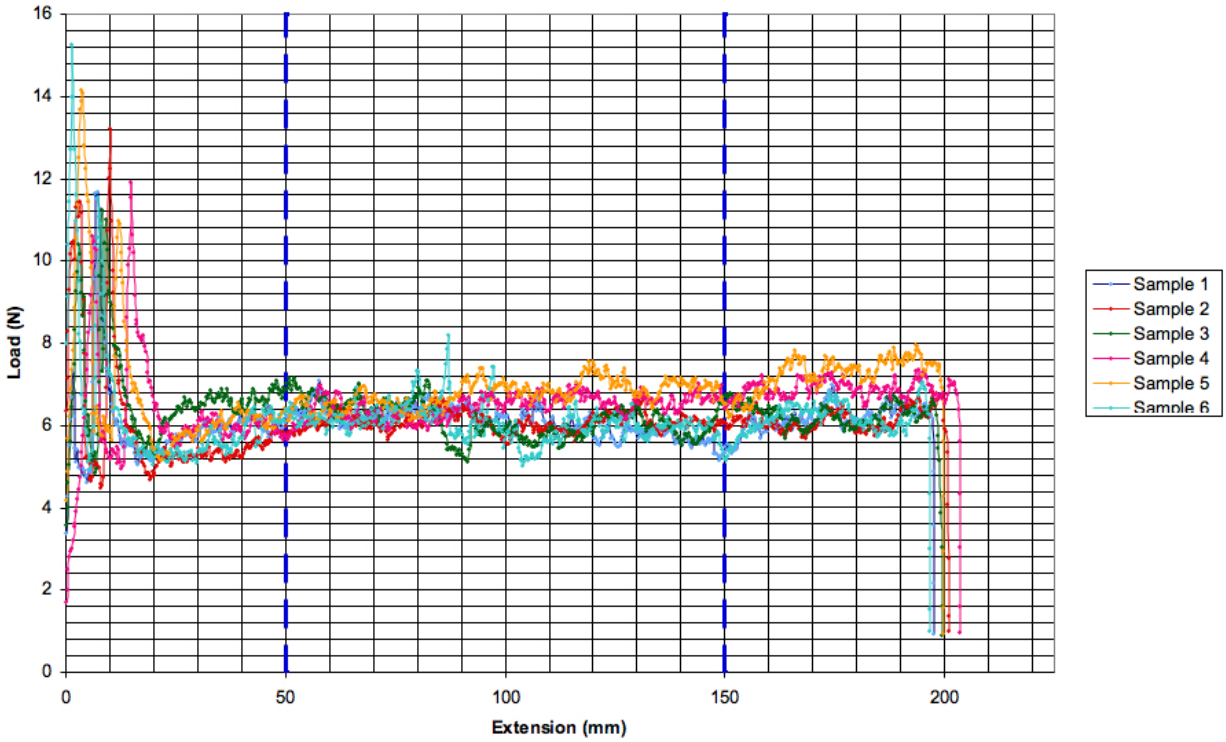


Fig. 17 Peeling Load (N) vs Extension (mm) for thermoset baseline AF563

As mentioned earlier, the mean value of the six peel strengths is calculated along with the standard deviation. All the results that fall outside the range ± 1.75σ (90% of the values) are excluded, as they are considered outliers. The detailed description of the baseline results is given in Table 6. In addition to the thermoset baselines, another test has been done in order to establish the parent material durability. The intention is to measure the peel strength intrinsic to the material. In other words, the adhesive strength between plies of the substrate. The value obtained by the parent material durability is 0.918 kN/m. It is reasonable to believe that this is the greatest value we could achieve with and adhesive film on our epoxy-based material, because in the case of an extremely strong adhesive, the adherend will start failing before the adhesive, that is when the load reaches a value equivalent to 0.918 kN/m.

Table 6 Parent material durability and baseline

Sample	Average Peel Strength (kN/m) ± 1.75σ (90%)		Process			Average Thickness (μm) ± 20μm	
			Soak Temp.	Soak Time	Pressure		
	Data	Outlier	°C	min	psi	before	after
Parent Material Durability							
T800S/3900-2	0.918	-	180	130	85	-	-
Baseline							
AF 563M	0.494	-	135	90	vacuum[1]	254	207
FM 300K	0.559	-	152	240	vacuum[1]	200	141

1, vacuum pressure is 0.96 bar (14 psi)

Making a quick comparison of the peel strength achieved with carbon fiber / epoxy prepreg, as compared to aluminum substrate; Cytec Engineered Materials achieve a peel strength of 4.0 kN/m with anodized aluminum, and the use of a primer BR 127. This is just to give an idea of were the adhesive properties of composites lie as compared to aluminum. The high peel strength of the adhesive with aluminum are due to the anodizing treatment which dramatically increases surface area, by offering and oxide layer with a great micro porosity, and also due to the primer which enhances bonding.

4.2.2 High peel strength of the ionomer and promoter

The ionomer S1856 and the Ethylene Metacrylic Acid (EMAA) used as adhesive films both have a very low melting point (below 100°C), which offers low service temperature and limits their application. However they are still tested, because their peel strength properties are very promising. Their process details are listed in Table 7. In fact, the S1856 and the EMAA have average peel strength of 1.185 and 1.789 kN/m respectively. This value is surprising as it is above the parent material durability of the T800S, and therefore it is expected that the adherend would fail before the adhesive. This phenomenon can be explained by the high elongation properties of the S1856 and the EMAA. During peel testing, the adhesive is usually sufficiently stiff, and does not elongate, therefore the failing surface can be approximated to a line across the width of the sample. However, when the adhesive elongates considerably, which is the case of S1856 and EMAA, the adhesive will not fail until it is stretched to a certain extent. In

this case the failing area can no longer be approximated by a line across the width, as it is now a whole surface area. Therefore the load being applied on the specimen is supported by a defined area instead of a width. For this reason, the adhesive can support a load, which exceeds the parent material durability. Although the high elongation of some thermoplastics gives higher peel strength, it is undesirable for shear properties, as described in more details later on. In fact common adhesives are relatively stiff, which gives them high strength in shear properties.

Table 7 Peel strength and processing of S1856 and EMAA

Sample	Average Peel Strength (kN/m) ± 1.75σ (90%)		Process			Average Thickness (μm) ± 20μm	
			Soak Temp.	Soak Time	Pressure		
	Data	Outlier	°C	min	psi	before	after
Thermoplastics							
Ionomer S1856	1.185	-	175	60	vacuum[1]	50	46
EMAA N1207C	1.789	-	175	60	vacuum[1]	50	43

1, vacuum pressure is 0.96 bar (14 psi)

4.2.3 Different failure modes

The nature of the failing mode is intrinsic to the adhesive and does not depend on the way the testing is performed. It mainly depends on the adhesive strength of the film, and its elongation properties. As we have previously seen the S1856 and the EMAA have high elongation properties, and this usually results in a cohesive failure. When the stiffness of the adhesive is a lot lower than the adherend, then it will start to stretch at a low force, and carry the load as the force increase. Therefore failure finally occurs within the adhesive film itself (cohesive) and the peel strength values are usually high, due to the "surface effect" described previously. An image of the failed surface along with a brief description is given in Table 8.

Adhesive failure occurs at the interface between the adhesive and the adherend. In the samples tested for this project, adhesive failure has only been seen at the interface with the flexible adherend and never with the rigid adherend. Adhesive failure shows low adhesion properties of the film and usually gives low values for the peel strength experiment.

Eventually when there is a strong adhesion of the film, failure occurs within the adherend itself instead of within the film. Both failures within the flexible adherend and the rigid adherend have occurred in this project. Failure within the flexible adherend shows good bonding, and is what has been observed for the thermoset baseline. The values for the peel strength are higher than adhesive failure, and usually close to the thermoset peel strength. However they do no match to the parent material durability strength, because only part of the single ply is being peeled off, not like delamination. On the other hand failure within the rigid substrate shows much higher values, somewhere close to the parent material durability strength. See Table 8 for a summary.

Table 8 Summary of the different failure modes

Failure mode	Description
Cohesive	Cohesive failure occurs because of high elongation of the adhesive film, it shows good bonding properties, and usually gives high peel strength value due to the “surface effect”. It is expected to show low shear resistance.
Adhesive	Adhesive failure shows low adhesion properties of the film and usually gives low values for the peel strength experiment.
Within flexible adherend	Failure within the flexible member shows good bonding, and gives values higher than adhesive failure, but not close to the parent material durability. Note that the fibers on the failed surface are oriented lengthwise as the flexible member.
Within rigid adherend	Failure within the rigid member shows highest values, similar to the parent material durability. In this case the adhesive strength is not being tested appropriately, as the values reflect the parent material’s intrinsic peel strength. Note that the fibers on the failed surface are oriented widthwise as the outermost ply of the rigid member.

4.2.4 Effect of failure mode on peel strength

As a general trend, the thermoplastic with high elongation showed a cohesive failure, while the thermoplastics with stiffness approaching the one of thermosets, showed the same failure mode as the thermosets; that is, failure within the flexible member. For every set of samples, the same failure mode was noticed for all 6 specimens, except for the PA12 N and PA12 S family. As a matter of facts, two or three specimen from the lot would show failure within the rigid member. In this case the peel strength would be similar to that of the parent material durability, because the rigid member is experiencing the same failure between laminates. Therefore it was considered that theses results were not representative of the adhesive strength of the thermoplastic film, and were excluded as outliers. The reason for such failure might be due to the initiation of the test, in which the first ¼ inch has to be manually peeled off in order to be able to place the rigid member on the mandrel. If the crack is initiated within the rigid substrate, the peel test is going to go along that crack. Although less energy would be required to peel the specimen with failure in the flexible member, there is an energy jump required to switch failure mode, so once it starts in the rigid member it is easier for the failure to continue its path, than it is to change failure mode.

The graphical representation of the peel tests results from the PA12 N0 is shown in Fig. 18 in order to illustrate this phenomenon. On the graph, all the samples, excluded 5 have a failure mode within the flexible adherend. The failure within the flexible adherend gives an average value of 0.591 kN/m, while the average peel strength for sample 5 is 1.370 kN/m, which reflects the parent material durability strength.

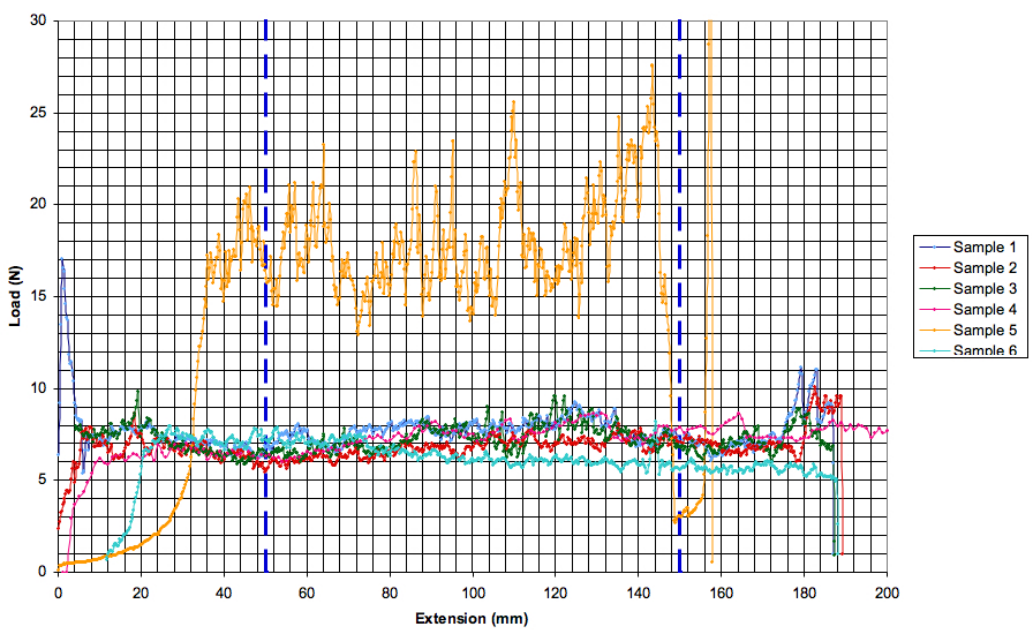


Fig. 18 Peeling Load (N) vs Extension (mm) for thermoplastic PA12 N0

Another interesting lot of samples to look at is the thermoplastic PA1285 S15, in which three different scenarios occurred. Fig. 19 b) shows the load vs extension curves for the three different failure modes. Sample 2 and 3 represent failure within the flexible adherend and the rigid adherend respectively. However sample 1, shows different failure modes over time. As can be seen in Fig. 19 a), by looking at the direction of the fibers on the failed surface, the sample started peeling in the rigid substrate. In fact at the beginning of the graph the load for sample 1 matches sample 3 (failure in the rigid adherend). Then, the first ply of the rigid member is been torn off from the substrate, in such a way that one end remains attached to the flexible member, and the other end is attached to the rigid substrate. Therefore the force applied is now being transferred to two different areas, so the specimen can support twice as much force. This explains why the value of sample 1 in the second part is twice as high as in the beginning. Then the surface failure switches to the flexible membrane, and at this point, the peel strength drops to the same value of sample 2 (failure in the flexible membrane).

a)

b)

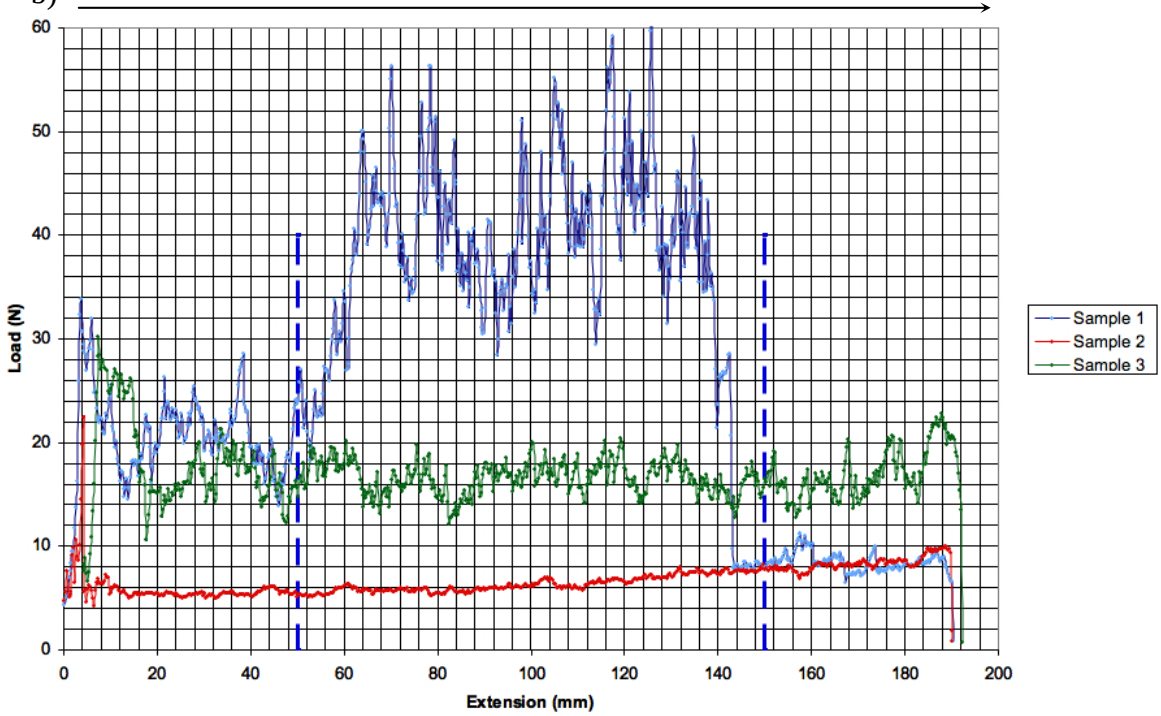


Fig. 19 a) surface failure and b) peeling load vs extension for thermoplastic PA1285 S15

When comparing PA12 N0 and PA1285 S15, we can see that the failure within the rigid adherent requires a similar load (around 18 N), however the load required for failure in the flexible adherend is different. This is also seen for other specimens in which failure occurs within the rigid adherend, and therefore confirms that failure within the rigid adherend doesn't represent the adhesive strength. Only when failure occurs within the flexible member, values can be compared.

4.2.5 General interpretation

A summary of all the results from peel test experiments is displayed in Table 9. The average peel strength for thermoplastic PA1270 S30 has been hard to establish since the failure mode is a combination of adhesive failure and failure within the adherent as shown in Fig. 20. The graph showed an oscillating nature, in which the high peeks are caused by the failure within the rigid adherend, and the low points are due to the adhesive failure. Therefore for each sample the peel strength has been calculated from the minimum value for load (instead of using the average).

Table 9 Peel test results for thermosets and thermoplastics structural adhesive films

Sample	Average Peel Strength (kN/m) ±1.75σ (90%)		Process				Average Thickness (μm) ± 20μm		Failure Mode
			Soak Temp.	Soak Time	Pressure	Cooling			
	Data	Outlier	°C	min	psi	°C/min	before	after	
P. Material Durability									
T800S/3900-2	0.918	-	180	130	85	-	-	-	-
Baseline									
AF 563M	0.494	-	135	90	vacuum[1]	-	254	207	flexible[2]
FM 300K	0.559	-	152	240	vacuum[1]	-	200	141	flexible[2]
Thermoplastic Films									
Ionomer S1856	1.185	-	175	60	vacuum[1]	1.2	50	46	cohesive
EMAA N1207C	1.789	-	175	60	vacuum[1]	1.2	50	43	cohesive
PA 12 Alloy	0.767	-	180°C	60	vacuum[1]	1.2	30	36	flexible
PA12-Epoxidized SBC	0.648	-	185°C	60	vacuum[1]	1.2	220	165	flexible
PA12 N0	0.591	5	185°C	60	vacuum[1]	1.2	270	246	flexible[2]
PA1285 N15	0.563	3,4,5	185°C	60	vacuum[1]	1.2	270	274	flexible[2]
PA1270 N30	0.494	1,2	185°C	60	vacuum[1]	1.2	290	252	adhesive
PA1285 S15	0.538	1,3,6	185°C	60	vacuum[1]	1.2	250	203	flexible[2]
PA1270 S30	0.821[3]	3	185°C	60	vacuum[1]	1.2	280	261	adh./rigid
PA 6 Alloy	0.633	-	230°C	10	vacuum[1]	-	80	117	flexible
Thermoplastic Paste									
PA6-CPA (Paste)	0.827	-	230°C	10	vacuum[1]	-	188	117	cohesive

"flexible": failure within the flexible adherend, "rigid": failure within the rigid adherend
"adh./rigid": combination of both adhesive failure and within the rigid adherend
1, vacuum pressure is 0.96 bar (14 psi)
2, the outlier samples show failure within the rigid adherend!
3, calculated from minimum peel strength

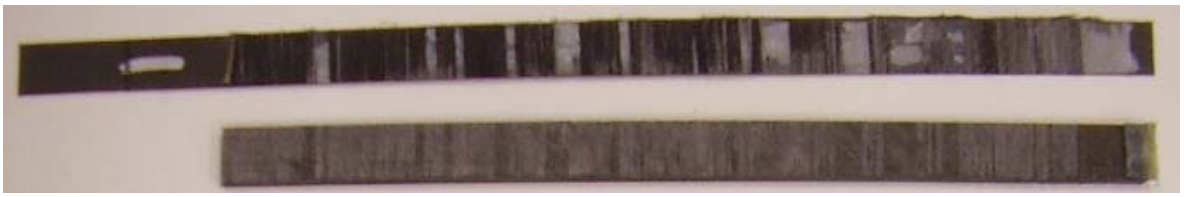


Fig. 20 Adhesive failure, and failure within the rigid adherend for specimen PA1270 S30

First of all, discarding both PA 6 which temperature is too high for application with epoxy-based resin, all our thermoplastic candidates show a peel strength similar or higher than the thermoset baselines. Although the ionomer S1856 and the EMAA show good peel strength, their low service temperature excludes their application in the aircraft industry, and concerns might grow when looking at the shear testing. On the other hand, the PA12 based thermoplastics all show a good potential in terms of peel strength. When looking at the PA12 films manufactured by hot pressing, adding the epoxidized group has improved adhesion. In the same way, the PA12 films doped with Na^+ ions has also improved adhesion. However it seems that the effect of the EMAA on the PA12 is minimized for the peel strength testing, especially for the non-doped PA12, where changing the EMAA content shows almost no effect. It is therefore necessary to look at the shear strength before drawing any further conclusions.

4.3 Shear Strength

4.3.1 Baseline results

The ASTM D1002-05 for the lap shear test recommends a total of 5 specimens per adhesive film, for the sample to be statistically correct. Most of the time 6 specimens were made for shear testing. For each sample, the load at failure is recorded, and is divided by the surface area of overlap, in order to get the shear strength in MPa. Similarly to the peel test analysis, for all six samples, the standard deviation is calculated, and the results outside the range $\pm 1.75\sigma$ (90%) are considered outliers. On average the standard deviation is quite low (around 1) which represents about 5% of the value for shear strength. Therefore our results are coherent and reproducible. Fig. 21 shows the load vs extension curves for the FM300 K adhesive film. The standard deviation for these results was 1.08 MPa.

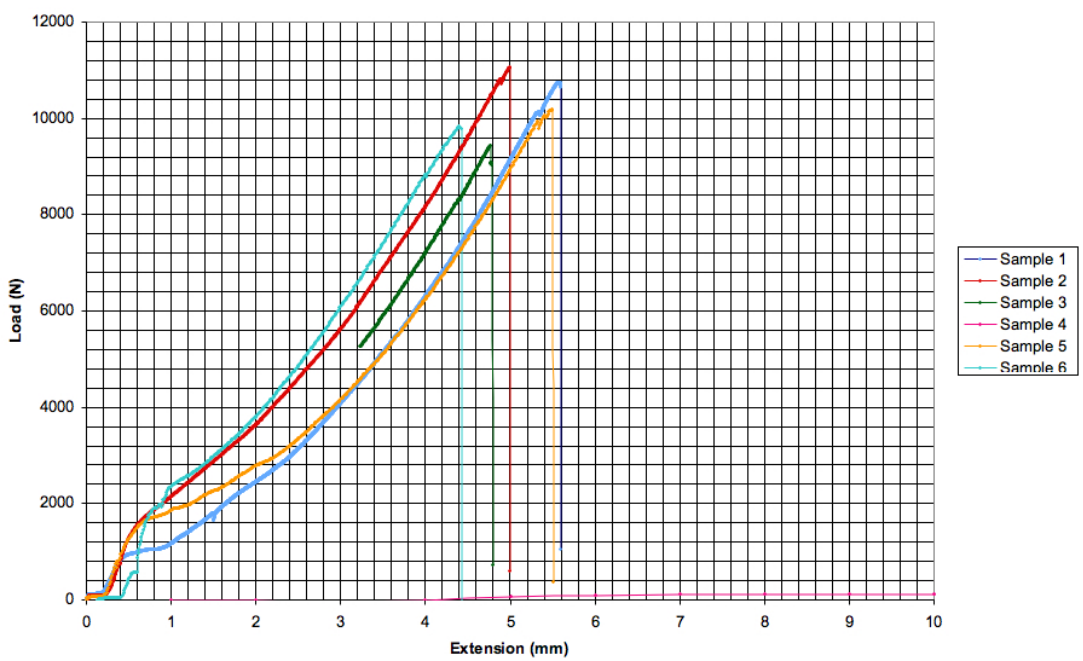


Fig. 21 shear load vs extension for thermoset FM300K

The shear strength results obtained for the baseline are displayed in Table 10. The average shear strength for AF563M and FM300K are 20.6 and 17.4 MPa respectively. The shear strength using epoxy-based composite materials is again smaller than the strength achieved with aluminum. For an anodized aluminum surface primed with BR127, Cytec Engineered Materials obtain a value of 36.8 MPa for the shear strength.

Table 10 Shear strength and processing of AF563M and FM300K

Sample	Average Shear Strength (kN/m) ± 1.75σ (90%)		Process			Average Thickness (μm) ± 20μm	
			Soak Temp.	Soak Time	Pressure		
	Data	Outlier	°C	min	psi	before	after
Baseline							
AF 563M	20.6	-	135	90	vacuum[1]	254	75
FM 300K	17.4	-	152	240	vacuum[1]	200	101

1, vacuum pressure is 0.96 bar (14 psi)

4.3.1 Different failure modes

For shear tests, two general failure mode have been experienced; cohesive failure and failure within the adherend. As mentioned earlier, for the thermoplastics film with high elongation properties, such as the ionomer S1856 and the EMAA, the failure mode will tend towards a cohesive failure, while the stiffer material will transfer the load onto the adherend, and failure will occur within the laminates. Fig. 22 shows the only three types of failure modes observed for shear testing, that is, cohesive failure, failure within the adherend, and a combination of both.

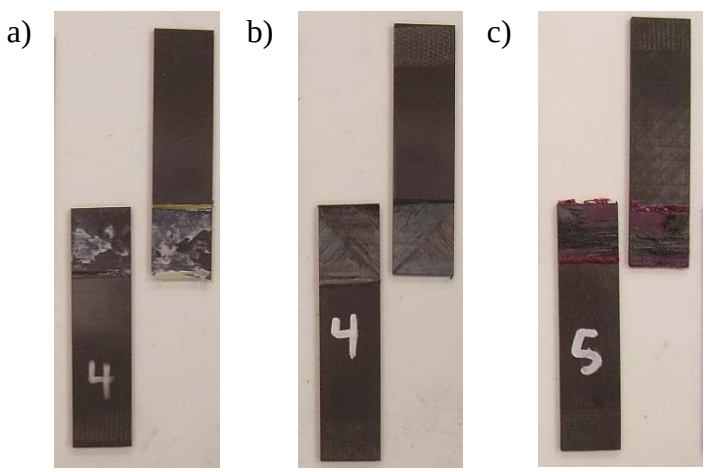


Fig. 22 Surface failure for the shear test, a) cohesive failure, b) failure within the adherend, and c) combination of both cohesive failure and within the adherend.

4.3.3 General interpretations

All the lap shear results are listed in Table 11.

Table 11 Lap shear test results for thermosets and thermoplastics adhesive films

Sample	Average Shear Strength (MPa) ±1.75σ (90%)		Process				Average Thickness (μm) ± 20μm		Failure Mode
			Soak Temp.	Soak Time	Pressure	Cooling			
	Data	Outlier	°C	Min	psi	°C/min	before	after	
Baseline									
AF 563M	20.6	-	135	90	vacuum[1]	-	254	75	cohe./adh.
FM 300K	17.4	-	152	240	vacuum[1]	-	200	101	cohe./adh.
Thermoplastic Films									
Ionomer S1856	11.8	-	175	60	vacuum[1]	1.2	50	46	cohesive
EMAA N1207C	8.6	-	175	60	vacuum[1]	1.2	50	50	cohesive
PA 12 Alloy	14.5	6	180°C	60	vacuum[1]	1.2	30	39	cohesive
PA12-Epoxidized SBC	20.6	6	185°C	60	vacuum[1]	1.2	200	65	adherend
PA12 N0	16.5	6	185°C	60	vacuum[1]	1.2	270	105	adherend
PA1285 N15	16.7	-	185°C	60	vacuum[1]	1.2	270	137	adherend
PA1270 N30	9.7	-	185°C	60	vacuum[1]	1.2	290	198	cohesive
PA1285 S15	15.5	-	185°C	60	vacuum[1]	1.2	250	108	adherend
PA1270 S30	11.5	-	185°C	60	vacuum[1]	1.2	280	106	cohesive

"cohe./adh." Failure mode is a mixture of cohesive failure and failure within the adherend
1, vacuum pressure is 0.96 bar (14 psi)

As was expected from the peel test results, the Ionomer S1856 and the EMAA show low shear resistance, mainly due to their high elongation property. Furthermore the failure mode observed for these thermoplastic is cohesive failure, for the same reasons described in the peel test analysis. Consequently PA12 based alloys with a high content of EMAA, that is PA1270 N30 and PA1270 S30 (30% EMAA) also show low stiffness and a cohesive failure. The shear strength values for the N30 and S30 along with the ionomer and the promoter (EMAA) are the four lowest shear values for thermoplastics and are almost half of the thermosets. Therefore a content of EMAA promoter greater or equal to 30% is to be avoided in the thermoplastics due to decreased shear resistance. Nevertheless adding only a 15% EMAA promoter is not sufficient to decrease significantly the shear resistance of the PA12 based thermoplastic. In fact PA N0 and PA1285 N15 have similar shear strengths of about 16 MPa. Furthermore when comparing the PA1285 N15 with the A1285 S15, little can be said about the effect of the Na^+ toughener in terms of both shear and peel tests. At last, the PA12 epoxidized Styrene Butadiene Copolymer (SBC) shows a very good shear resistance, in the same range as the thermoset baseline, also considering the fact that its peel strength is higher than the thermoset baselines.

4.4 Factors to consider

In this section it is relevant to mention the important parameters and factors, which influence final properties of the thermoplastics adhesive films. Although the aim of this project only concerns the first step in evaluating potential thermoplastics as adhesive films, and does not concern an extended study of the influence of different parameters on the film's properties, it is worth mentioning the parameters and factors which should be taken into account for eventual further studies on this topic. The most important variables are related to the processing cycle, such as dwell time and temperature, and the initial properties of the film, such as its original thickness prior to processing.

4.4.1 Dwell time and temperature

Although for thermoplastics the dwell time is not as critical as for thermosets, since there is no curing process taking place, it is still necessary to ensure a sufficient dwell time for the temperature profile to be homogenous throughout the film, and therefore to guarantee isotropic properties. In addition, the dwell time shouldn't be too long as it might start degrading the thermoset if held too long at high temperatures.

In order to involve as less parameters as possible in this project, the melting cycle for thermoplastics has been kept constant with a dwell time of 60 min, and a temperature ranging from 175°C to 185°C. However prior to establishing this dwell time, a run was made with only 10 min dwell time for several thermoplastics. To illustrate the influence of dwell time on the peel strength of the adhesive film, Fig. 23 shows the peel strength of EMAA in function of two different dwell times, 10 and 60 min. The peel strength more than doubles when dwell time is increased from 10 min to 60 min.

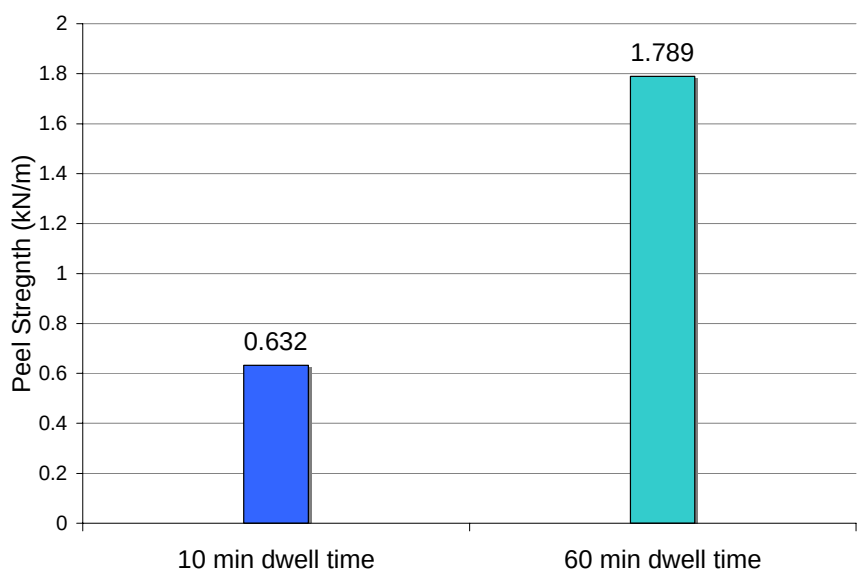


Fig. 23 Peel strength of EMAA thermoplastic melted at 175°C, for 10 and 60 min

4.4.2 Cooling rate

When processing a thermoset, the cooling rate of the temperature cycle doesn't matter, because at the end of the dwell time, the thermoset is already cured, in other words, cross linking is already established and the resin is solid. Therefore the speed at which the thermoset is cooled down will not significantly affect its properties. On the other hand, with a thermoplastic, and especially with semi-crystalline polymers, such as Polyamide, solidification is a whole different story. At the end of the soak time, the thermoplastic is completely liquid, and solidification will start as the temperature is dropped. As mentioned in section 3.3 the solidification of semi-crystalline polymers goes through the formation of crystals, which's growth rate depends on the cooling rate. Therefore different cooling rates will provide different proportions of crystals in the adhesive film. As we do not wish the cooling rate to become a variable in this part of the project, it has been kept constant by the default cooling rate of the oven. The cooling rate was recorded with a thermocouple and turned out to be 1.2°C/min.

4.4.3 Film thickness

Another important factor to consider and which hasn't been mentioned so far is the film thickness. The film thickness will definitely influence both the peel and shear strength. However the optimal film thickness will depend on the thermoplastic being used. There is no straightforward formula, which can an appropriate thickness to use for adhesive film. However the film thickness used for the thermoset baseline is 200 and 254 µm for the FM300K and the AF563M respectively. The initial thickness used for the thermoplastics varies from 30 µm to 300 µm. In order to give a general idea, Fig. 24 gives the a) peel and b) shear strength of the adhesive films along with their thickness after processing (in gray).

Fig 24 a) peel strength and thickness of adhesive films

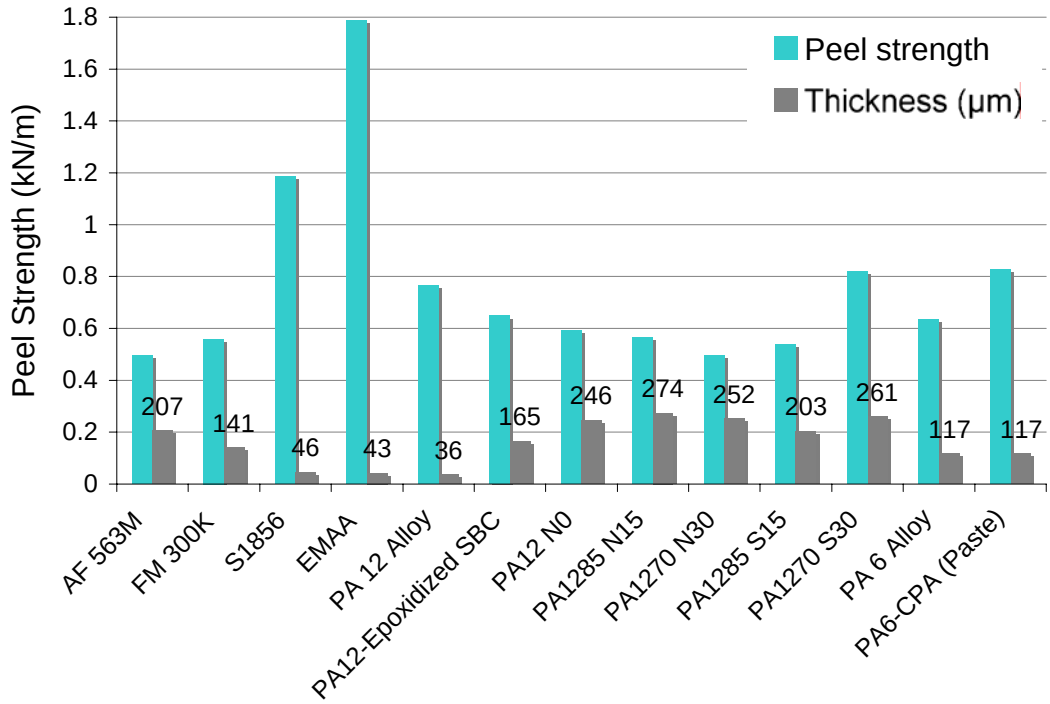
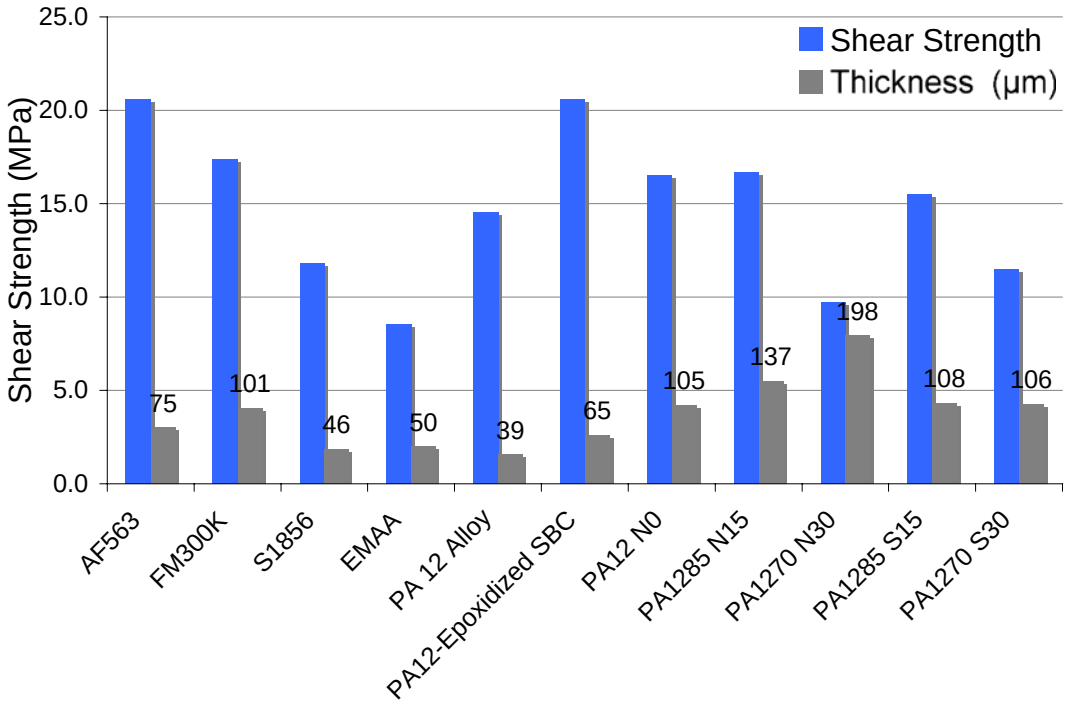


Fig 24 b) shear strength and thickness of adhesive films



For both the peel and shear test it seems that there is a general relationship, in which the thinner the film, the higher the strength. In other words thin films tend to do better than thicker ones in both peel and shear testing. However this trend cannot be generalized based on these results. Further study needs to be made considering the same type of thermoplastic with different thicknesses.

4.5 Candidates with great potential

In evaluating the potential list of thermoplastics for structural adhesive we have first looked at films with high adhesive properties such as the Ionomer S1856 and the EMAA promoter, which in fact have shown good peel resistance, but unfortunately showed poor service temperature for their application in the aircraft industry. Polyamide based thermoplastics have shown some good properties in both peel and shear strength. However, the addition of the EMAA promoter seems to be beneficial only when added in small quantities (15%). Out of all the Polyamide selection, 3 thermoplastics in particular show similar characteristics in the same range as the baseline thermoset, for both peel and shear test. The PA N0, PA1285 N15 and the PA12-epoxidized SBC (see Fig.25). The PA12-epoxidized SBC in particular overcomes the requirements defined by the thermoset baselines and shows slightly higher values in both cases. Although further studies need to be made in order to meet all other criteria, there is a great potential for the PA12-epoxidized SBC in the use of structural adhesive for the aircraft industry.

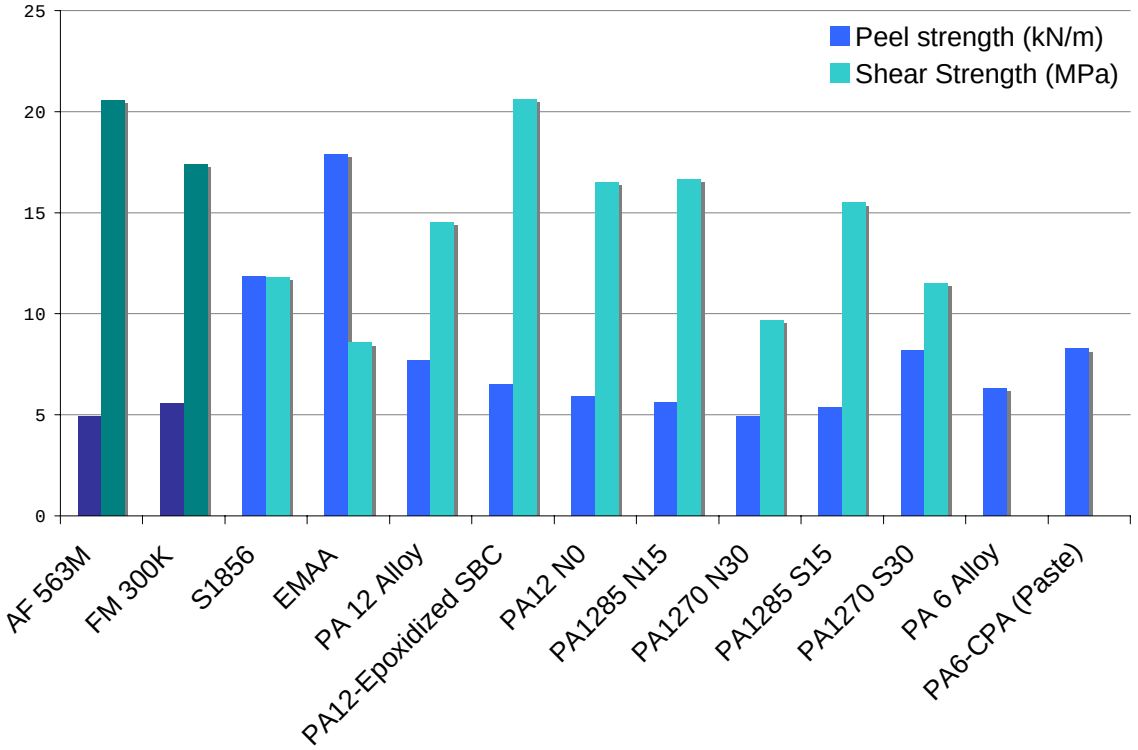


Fig. 25 Peel strength and shear strength for thermoplastic candidates (light) compared to the baseline (dark)

5. Further studies

5.1 Determining the influence of the parameters

As described earlier we have seen that the adhesive properties of the thermoplastics films depend on several parameters such as the dwell time and temperature, or also the thickness of the film itself. Once, one or more thermoplastic candidates will have been selected, the future objective for this project is to investigate the influence of the parameters mentioned previously, and to establish the optimal conditions for best performance of the adhesive film. Another aspect, which should be investigated, is the orientation of the fibers from the epoxy-based composite material with respect to the direction of peel. Because we have observed that in the peel test the fibers of the flexible adherend were going in the lengthwise direction, while the fibers of the rigid adhered in the perpendicular direction. And the failed surface analysis showed that the peel strength was different whether the failure occurred within the flexible adherend or the rigid adherend.

5.2 Future investigation

Further investigations on this project involve performing new test experiments to evaluate additional properties of the film in order to meet the requirements. These tests involve hot-wet lap shear tests, and creep. Creep properties show the elongation of the film over a long period of time, and submitted to heat. This helps evaluate the long-term reliability of the adhesive film and will be a crucial part for this project.

Furthermore another main investigation is being started right now, and concerns the applications of our thermoplastic on aluminum substrates. This is in relation to the PA 6 Alloy and the PA6-CPA paste, which showed good properties, but had a too high melting temperature for their applications in the epoxy-based composite sector. However when dealing with aluminum substrate we are no longer limited to a melt temperature of 180°C, and therefore the PA 6 group can find applications in this sector. We have currently prepared lap shear samples with AL 6061 substrate 0.125" thick. The aluminum substrate is being tested will all the thermoplastics used for the epoxy-based composite material and the thermoset baseline. For each thermoplastic, 3 cases have been distinguished; the first case in which unpolished aluminum is surface treated using sand blasting and cleaned with rymplecloth, the second case in which the unpolished aluminum is treated with the NAVAIR procedure used for the epoxy-based composite material, and finally the last case were the aluminum surface is anodized for adhesive enhancement. The later case is resomended by the aircraft industry, and consists of and FPL (Forest Products Laboratory) etching, followed by a Phosphoric Acid Anodizing (PAA). The anodizing on the aluminum creates an oxide layer with a high content of microscopic cavities, which provides a high surface area for bonding.

6. Conclusions

The capability of using thermoplastics as adhesives for thermosets materials has been evaluated using a wide range of thermoplastics based on their adhesive strength. Amongst other, a Na^+-based ionomer S1856 and an adhesion promoter EMAA have shown high peel resistance but poor shear strength due to the high elongation of these polymers. Therefore series of PA12 alloys have been tested some of which were doped with Na^+ ions for toughening, and other were alloyed with adhesion promoter EMAA. Another PA12 based epoxidized polymer was alloyed with Styrene Butadiene Copolymer (SBC). The results showed that a lower peel and shear resistance was achieved with a 30% EMAA promoter, while good resistance was seen with lower (15%) or no EMAA content. Little difference is seen between the 15% and the 0% EMAA PA12 alloys, for both the shear and the peel test. The influence of Na^+ toughening could not be established; as the samples showed similar values in both cases. On the other hand, The PA12-epoxidized SBC showed high peel and shear strength; 0.648 kN/m for the peel strength, and 20.6 MPa for lap shear tests. Both values are higher than the thermosets baselines (AF563 and FM300K), and therefore the PA12-epoxidized SBC shows great potential for structural adhesives.

Nevertheless, further studies such as hot-wet lap shear and creep testing need to be made in order to meet all the requirements. In addition further studies will be made on the influence of processing parameters such as dwell time and temperature on the adhesive properties of the thermoplastics. A study on the thickness of the film should also be made as it seems that the adhesion increases with thinner films for both lap shear and peel test.

References

[1] Center for Composite Materials (CCM), University of Delaware, Newark, DE19716-3144, URL: http://www.ccm.udel.edu

[2] Toray Carbon Fibers America, Inc. Technical Data Sheet No. CFA-019

[3] NAVAIR Technical Manual. Organizational and Intermediate Maintenance, General Composite Repair NAVAIR 01-1A-21, (p7-46)

[4] NAVAIR Technical Manual. Organizational and Intermediate Maintenance, General Composite Repair NAVAIR 01-1A-21, (p6-24)

[5] S. Black, Thermosetting Structural Adhesives, Composites Technology, June 2007