TOUGHENED EPOXY PASTE ADHESIVES FOR AEROSPACE APPLICATIONS

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SUMMARY

The production rate acceleration by aircraft manufacturers requires revolutionary changes in manufacturing processes and use of out-of-autoclave adhesives for structural and semi-structural parts. This paper presents a new toughened epoxy paste adhesive with long open time which is developed within the frame of the EU funded project ABiTAS.

Keywords: Two part epoxy paste adhesives, Composite bonding, Thixotropy, High Temperature, High Peel

1. INTRODUCTION

1.1. State of the art assembly technology – film adhesive / autoclave bonding

To produce the best wide-range temperature and vibration-resistant composite structures for aircraft, current technology usually uses vacuum-bagging of ambient temperature assembled layups, often in a clean room environment for maximize adhesion. State of the art adhesives for bonding of metals or CFRP are epoxy based films, which are typically cured at 120-180°C for 1-3 hours under pressure in an autoclave (3-7 bars). This achieves stable, high glass transition temperature (T_g), cured, epoxy-bonded composite assemblies with sufficient adhesion and crosslink density to withstand the subsequent assault of aircraft fluids and large temperature excursions. The wide temperature excursions occur in flight, depending on location on the aircraft, as well as during ground storage in the wide variety of weather conditions encountered over the year and around the globe.

1.2. Next generation assembly – paste adhesive / cold bonding

The needs for production rate acceleration by aircraft manufacturers to meet their delivery demands, as well as for faster repair operations to reduce AOG (Airplane on Ground) times, require revolutionary changes in both manufacturing and repair processes for structural parts. They need faster throughput, reduced labour costs, and increased energy efficiency, making it highly desirable to use easily stored, applied and cured paste adhesives, which don’t require rigorous clean room conditions, or autoclave curing.

The ABiTAS (Advanced Bonding Technologies for Aircraft Structures) project has as a central target the development of a novel process chain for the assembly by paste adhesive bonding of components contributing to both short (-20%) and long term (-50%) cost reduction following the ACARE recommendations.

1.3. Next generation assembly – toughened structural paste adhesive

First and second generation epoxy adhesives tend to be either high temperature adhesives (perform well in hot lap shear conditions) or high peel adhesives (give good peel performance) as presented in Figure 1.

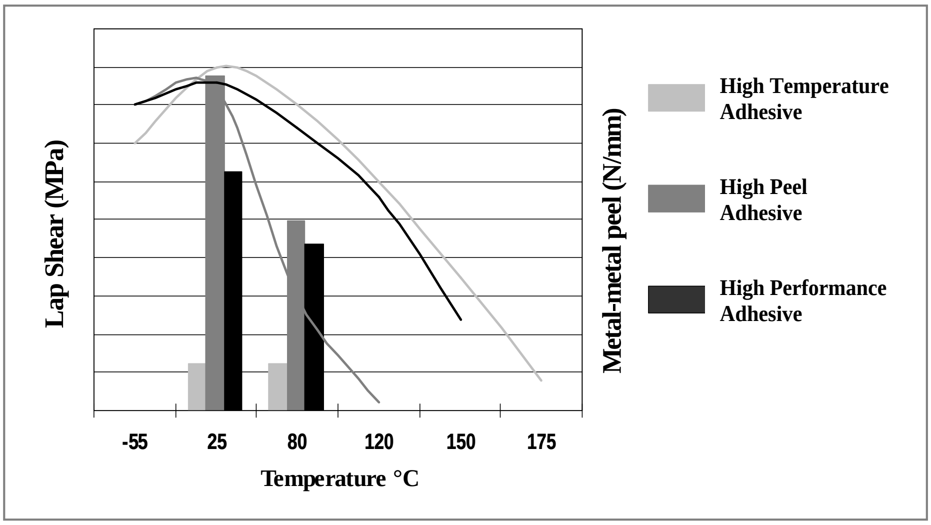

Figure 1: Schematic presentation of the lap shear/peel performance of different types of epoxy adhesives

The adhesive LMB 6687-1 / LME 10049-3 developed within the ABiTAS project combines the high temperature performance of a high temperature adhesive with the peel performance of a high peel adhesive (presented in Figure 1 as High Performance Adhesive). This has been achieved by a desired cured morphology of the paste matrix showing high mechanical performance with lap shear and peel strength above 30 MPa and 7 N/mm, respectively.

Additionally the new adhesive exhibits high hot/wet Tg, long open time (up to 3 hours as a result of reduced carbonation) needed for large part assembly and a rheology suitable for mix dosing dispensing with non-slump behaviour up to 2-3 mm adhesive application.

2. RESULTS AND DISCUSSION

2.1. Application

2.1.1. Processing

In the view of reducing manufacturing time, one of the ABiTAS objectives is to dispense paste adhesive by an automated process such as mix dosing equipment. The paste adhesive is also required to have such as rheology (non slump) enabling vertical application of bond thickness up to 2-3 mm.

In Figure 2 is represented the viscosity against shear rate of the single components which is representative of the behaviour of the mixed adhesive. Both components have on one hand low viscosity at high shear rate necessary to ensure homogeneous mixing in the mixing chamber and on the other hand high viscosity at low shear rate (thixotropic behaviour) to enable application on vertical surface.

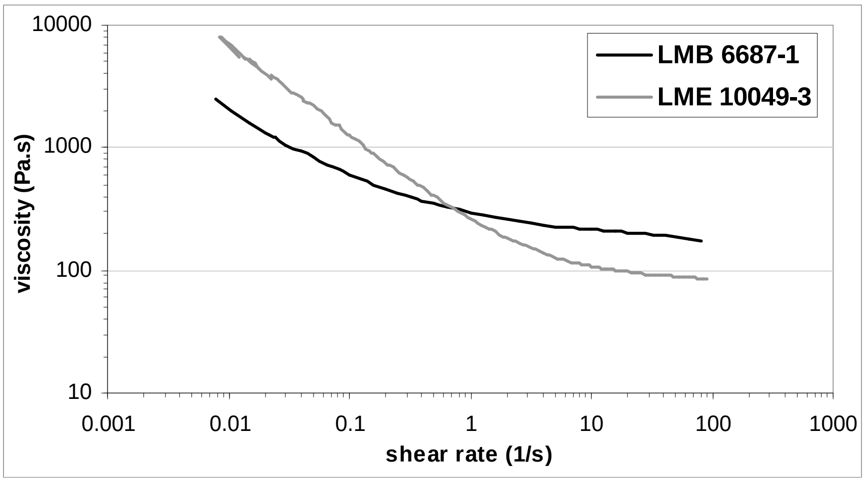

Figure 2: Viscosity against shear rate of single components

Slump test performed on the mixed adhesive show that LMB 6687-1 / LME 10049-3 is suitable for vertical adhesive bonds up to 2-3 mm.

2.1.2. Assembly time

The open time of an adhesive is the time elapsed between the moment the A and B component of the adhesive system are combined and thoroughly mixed and the completion of the assembly for bonding providing:

- the viscosity / rheology of the adhesive is good enough to squeeze and wet the adherents properly,
- the properties remain unchanged after such an open time compared to 0 min open time. For instance environmental conditions such as humidity induce a modification of the adhesive surface (carbonation) that can result in a drop of the performance.

In Figure 3 is represented lap shear performance of LMB 6687-1 / LME 10049-3 after 1, 2 and 3 hours open time at room temperature. Conventional adhesives are either too reactive (fast viscosity increase) or prone to carbonation which make them only suitable for fast assembly.

The combination of controlled reactivity and reduced carbonation in LMB 6687-1 / LME 10049-3 allow the bonding of large parts with assembly time up to 3 hours. The fracture mechanism of the LSS coupons is cohesive whatever the open time and is further evidence of the reduced carbonation effect.

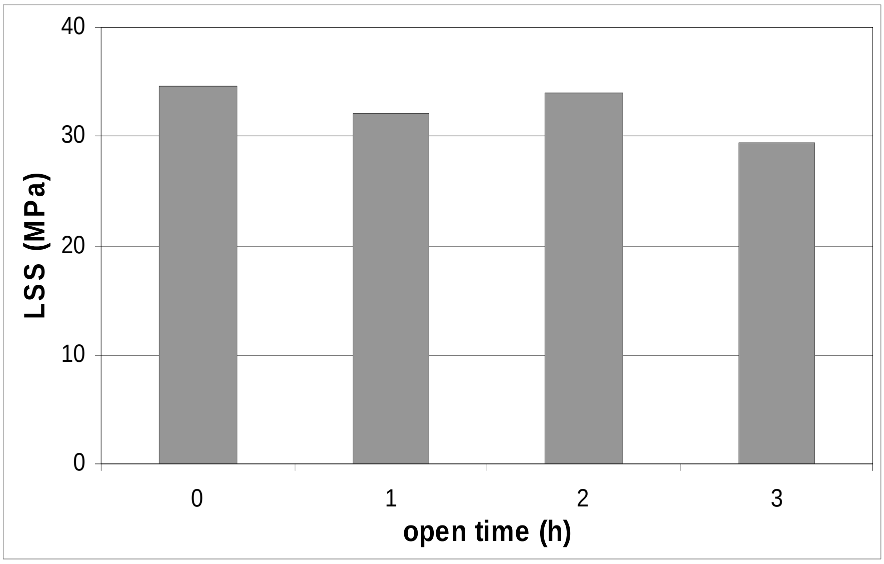

Figure 3: Open time measurement as a function of lap shear strength retention

2.1.3. Cure profile

Figure 4 shows the cure conversion (EN 6041-6) of LMB 6687-1 / LME 10049-3 after several cure cycles. Each of the cure cycle is preceded by a room temperature gelling stage of at least 4-6 hours to enable the part to have enough green strength to be manipulated.

For structural applications where > 95% conversion is required, 80°C is seen as the minimum cure cycle temperature. Higher cure temperature (100°C) can be used to shorten cure time.

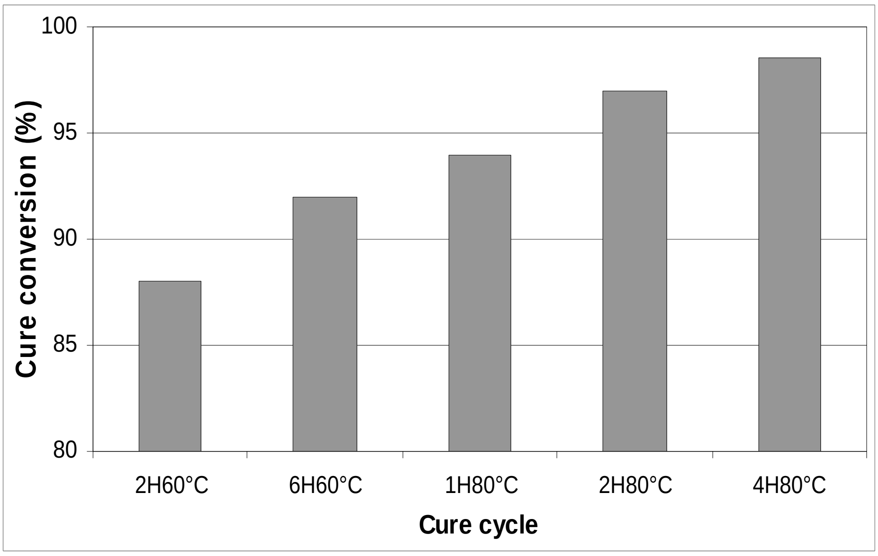

Figure 4: Cure conversion versus cure cycle

2.2. Mechanical Performance

2.2.1. Strength Performance

Table 1 shows lap shear strength (LSS) of LMB 6687-1 / LME 10049-3 on chromic acid etched Al 2024T3 and CFRP UD 8552. The surface of the CFRP is prepared by the wet abrasion technique. LSS values were measured per EN 2243-1, 0.3 mm bondline calibrated with 0.5wt% glass beads after RT gellation followed by curing for 4 hours at 80°C.

Table 1: LSS data of LMB 6687-1 / LME 10049-3

Test Temp (°C)	**Substrate**	**LSS (MPa)**	**Fracture**
-55	Al 2024 T3	45.8	CF
23		34.7	CF
80		22.6	CF
120		13.3	CF
23	CFRP UD 8552	27.60	CF / AF / DF
80		15.33	CF / AF / DF

LMB 6687-1/LME 10049-3 has high ambient and sub-ambient lap shear strength on aluminium with 65 % and 35% retention of LSS at 80°C and 120°C respectively. The fracture mechanism is cohesive (CF) over the whole temperature range.

The LSS on CFRP are preliminary values and have to be considered as minimum. Indeed the single lap shear geometry is not well adapted to CFRP due to the occurrence of peel forces during the test inducing bending of the laminates. As a result the fracture mechanism is a combination of cohesive, adhesive and delamination failure.

2.2.2. Toughening Performance

Table 2 shows peel data and interlaminar fracture toughness energy (G_1C) of LMB 6687-1 / LME 10049-3 on chromic acid etched Al 2024T3 and CFRP UD 8552 respectively. The surface of the CFRP is prepared by the wet abrasion technique. Roller peel and T-peel were measured per EN 2243-2 and ASTM D1876. G_1C was measured per AITM 1.0005. The maximum load represented in Figure 5 is the maximum load observed after the precrack is made. Bondline is 0.3 mm calibrated with 0.5wt% glass beads and specimens cured for 4 hours at 80°C after a gellation stage at room temperature.

LMB 6687-1/LME 10049-3 has high ambient and sub-ambient roller peel with cohesive failure. It also has a high T-peel with a failure being 80% cohesive (CF) and 20% adhesive (AF). The difference in fracture mode from roller to T-peel is often observed as the higher peel angle is more likely to induce adhesive failure.

Table 2: Toughness data of LMB 6687-1 / LME 10049-3

Test Temp (°C)	**Test**	**Standard**	**Unit**		**Fracture**
-55	Roller Peel	EN 2243-2	N/mm	7.6	CF
23				7.9	CF
23	T-Peel	ASTM D1876		4.8	CF / AF
23	G_1C	AITM 1.0005	J/m^2	1840	CF / AF / DF

It also has an impressive interlaminar fracture toughness energy of 1840 J/m^2 with a precrack load of about 250 N. The fracture mechanism on the CFRP is a mixed mode of cohesive, adhesive and delamination failure. The distribution of the fracture is inhomogeneous along the specimen as it goes from cohesive within the first 5 cm crack to adhesive and delamination failure. Such a phenomenon is likely to be due to laminates being more prone to fiber delamination as the crack angle and the bending of the laminate both increase as the crack propagates.

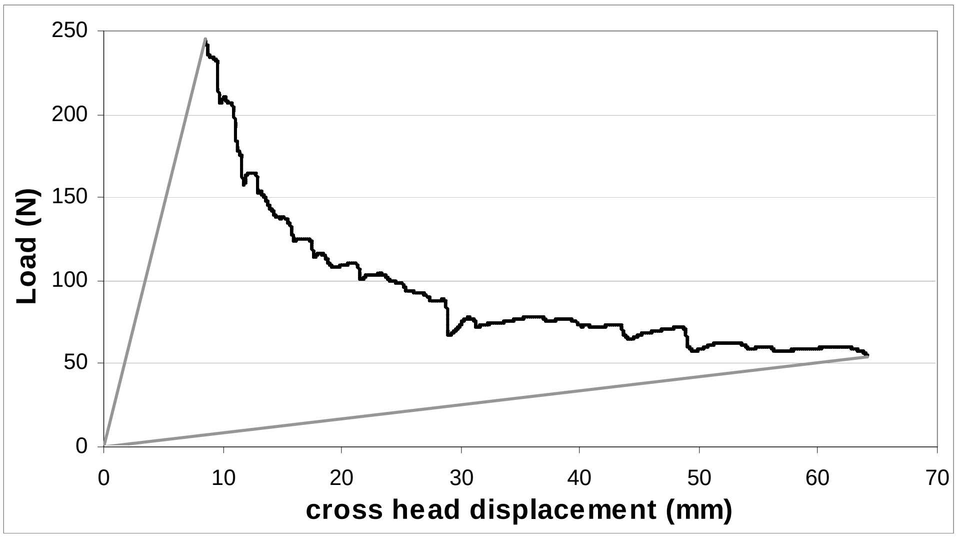

Figure 5: Interlaminar fracture toughness energy (G_1C) of LMB 6687-1 / LME 10049-3

The high level of toughness is given by the combination of a high crosslinked / Tg network with a desired cured morphology as shown in Figure 6. Indeed the dispersed phase has a bimodal distribution with a first population of 1-3 microns diameter spherical domain and a second one of 100-400 nanometer.

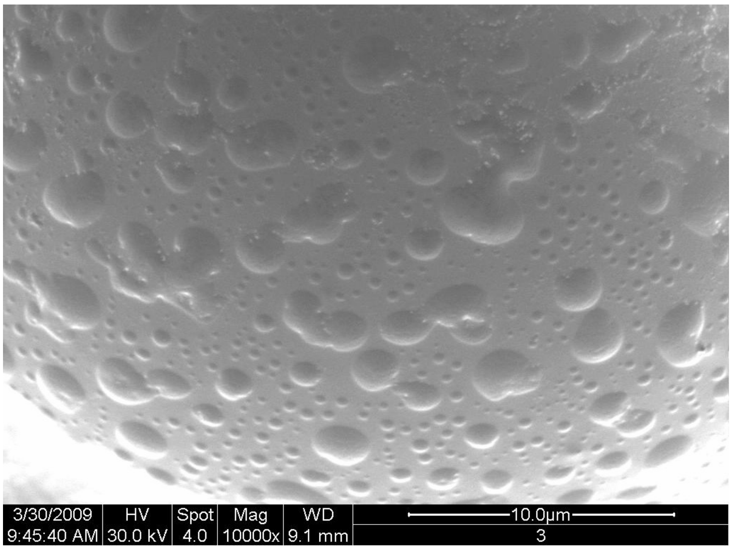

Figure 6: SEM picture of the bimodal distribution of the dispersed phase

2.2.3. Hot/Wet performance

In Figure 7 is shown the DMA of LMB 6687-1 / LME 10049-3 after curing 4 hours at 80°C (after gelling stage at room temperature). Samples were measured both dry and after wet conditioning at 100°C (in boiling water) for 72 hours. Such hot/wet conditions are used to generate quick data and are more severe than the standard water saturation at 70°C/85% RH.

LMB 6687-1 / LME 10049-3 has a Tg onset DRY of 92.5°C and a Tg onset WET of 103.5°C. Apart from the fact that there is no decrease in Tg, another important factor is that there is no evidence of hydrolytic degradation of the network. Indeed the glassy plateau is smooth till the glass transition.

In some conventional adhesives, though the main Tg is increased, part of the network is subjected to hydrolitic degradation resulting in the appearance of another transition at lower temperature. In other words the Tg DRY is split into 2 Tg's after hot/wet conditioning.

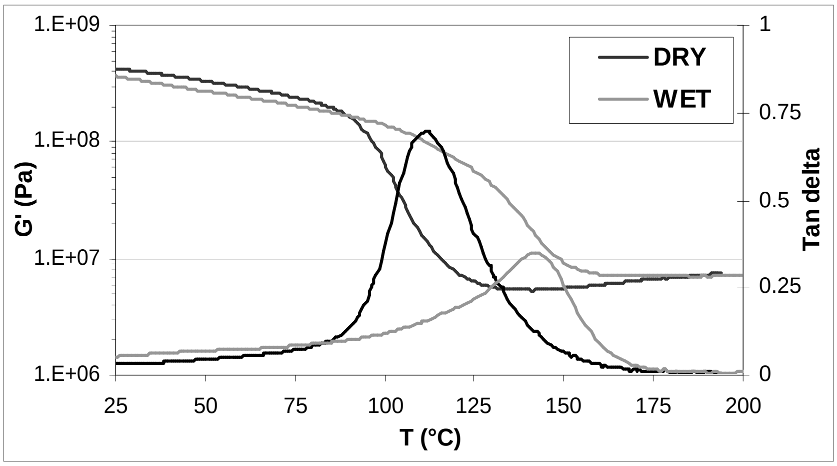

Figure 7: DMA of LMB 6687-1 / LME 10049-3

3. CONCLUSION

The combination of a highly crosslinked / high Tg network with a desired cured morphology leads to an adhesive exhibiting high mechanical performance with lap shear and roller peel strength on aluminium above 30 MPa and 7 N/mm², respectively.

The first set of data on composites is very promising with an interlaminar fracture toughness energy of 1840 J/m^2.

The high hot/wet Tg should confer the adhesive good retention of the mechanical performance after environmental conditioning.

The combination of ease of application (processing by mix dosing, long assembly time, medium temperature cure profile) and wide-temperature-range mechanical performance makes LMB 6687-1 / LME 10049-3 a promising candidate for aerospace structural application and more specifically as a replacement of structural film adhesives.

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