UPDATING THE MAPSIL® 214 BV PRODUCTION PROCESS

G. Sierra [(1)], D. Sacramento [(1)], S. Solé [(1)], O. Guillaumon [(1)]

[(1)] MAP, ZI - 2 Rue Clément Ader, 09100 Pamiers, France, g.sierra@map-coatings.com

ABSTRACT

MAPSIL® 214 is a low outgassing encapsulating silicone resin developed in the 1980s using a liquid-liquid purification process developed by CNES.

The MAPSIL® 214 production process has been updated in order to eliminate the use of organic solvents in the purification process.

This paper summarizes the validation tests which have been done so far to characterize the new version of MAPSIL® 214 BV. All the properties were compared to the current version of MAPSIL® 214 BV.

1. INTRODUCTION

Since its creation in 1986, MAP has developed numerous products for the space industry. Most of these products are silicone-based greases, adhesives, varnishes or coatings.

MAPSIL® 214 is a low outgassing encapsulating silicone resin obtained via a liquid-liquid purification process (patented by CNES) that makes it possible to obtain degassing values compatible with space applications [1].

In order to end the use of organic solvents that do not comply with new European environmental regulations (REACH), the purification process has been modified.

Until now, two versions of MAPSIL® 214 were available: MAPSIL® 214 BV and MAPSIL® 214 HV, which were developed to fit the uses regarding the viscosity. MAPSIL® 214 BV stands for low viscosity (10 Pa.s) and MAPSIL® 214 HV for high viscosity (350 Pa.s). Finally, it was decided to keep only one version, similar to the MAPSIL® 214 BV.

In order to check the properties of the new version of MAPSIL® 214 BV, we have defined the following qualification plan:

1. Control of the product at initial stage and comparison of the properties of the new version of MAPSIL® 214 with the current one;
2. Ageing tests.

This paper first presents the properties of the new version of MAPSIL® 214 BV at initial state. These properties are compared to those of the current version. Secondly, the results after ageing tests are presented.

2. MATERIALS, PROCESSES AND TECHNIQUES

2.1. Materials

MAPSIL® 214 is a two-component RTV-2 silicone elastomer. The base is a mix of silicone polymer, pigments and several additives which give it its rheological and mechanical properties. The hardener is composed of a mix of silicone cross-linker and additives to adjust the viscosity. Base and hardener are 100% solids content products. In order to reach the low outgassing rates as defined by the ECSS [1], a solvent-free purification process was used instead of the purification process based on the use of solvents used until now.

To obtain the final material, it is necessary to mix the base and the hardener in the respective weight proportions of 100 to 10. The standard curing process corresponds to (1) 8h at 65°C whereas an alternative one is (2) 7 days at 23°C and 55% relative hygrometry (RH). The chemical reaction gives a final elastomer. The main characteristics of the current elastomer [2, 3] are listed in Tab.1.

Table 1. General properties of current MAPSIL® 214 encapsulating silicone resin cured at 65°C for 8 hours

MAPSIL® 214 Current version	BV	HV
Density	1.25	1.25
Viscosity at 50 s^{-1} (Pa.s)	10	350
Pot-life (min) at 20°C	120	120
Hardness (ShA)	35	50
TML (%)	0.24	0.18
RML (%)	0.23	0.17
CVCM (%)	0.04	0.04
Electrical surface resistance (Ω/□)	$>10^{12}$	$>10^{12}$
Electrical resistivity (Ω.cm)	$>10^{14}$	$>10^{14}$

2.2. Techniques

Outgassing rates are measured further to ECSS-Q-ST-70-02C standard [1]. The measurements were taken at Airbus Toulouse.

The linear coefficient of thermal expansion (CTE) of the sample was measured by Thermomechanical Analysis (TMA) further to the ISO11359-2 standard [4]. This means of measurement is directly derived from dilatometer and involves an oven with a sample holding system positioned inside. This system consists of a tray and a silica pusher for standard expansion mode or a setting system tension of samples consisting of a silica frame and two jaws in tension mode. These systems of gripping the samples make it possible to follow the movement of the ends of the sample during a ramp in temperature. It is this displacement measurement that allows the calculation of the coefficient of thermal expansion.
The linear coefficient of thermal expansion was measured using TMA. The measurements were carried out by ELEMCA using a TMA 402 F1 NETZCH under helium.

Thermal conductivity is measured using the flash laser method. This method is adapted to solids thermal conductivity measurement [5].
A sample is heated on one of its faces by laser irradiation, on the other side a measurement of temperature as a function of time by pyrometry is carried out. The analysis of the thermogram obtained on the rear face of the sample makes it possible to determine the thermal diffusivity of the sample.
Different models make it possible to analyze these thermograms and to deduce the thermal diffusivity, among them the simplest is the adiabatic model represented above [5]:

Eq.1 $$a = 0.1388\ x\ \frac{e^2}{t_{0.5}}$$

Where a is the thermal diffusivity [$mm^2.s^{-1}$], e is the thickness of the sample [mm] and $t_{0.5}$ is the "half rise" time, at 50% of the temperature rise of the rear face of the sample [s] (IR sensor side).
The thermal diffusivity measurements are made using a Netzsch LFA 457 diffusivimeter on samples ranging in thickness from 1.2 to 1.9 mm.

Knowing the diffusivity, we may go back to the value of its conductivity using the following equation:

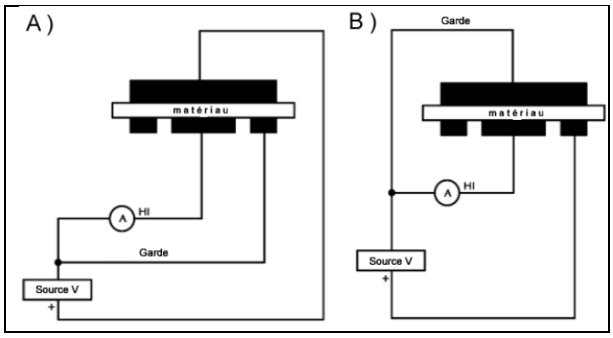
Eq.2 $$\lambda = a\ x\ \rho\ x\ C_p$$

Where λ is the thermal conductivity [$W.m^{-1}.K^{-1}$] and a the diffusivity [$m^2.s^{-1}$], ρ and Cp correspond respectively to the density of the sample [$kg.m^{-3}$] and its mass heat capacity [$J.kg^{-1}.K^{-1}$].

The density measurements were carried out by double weighing using the Archimede's principle and the mass heat measurements on a SETARAM calorimeter.
The measurements were performed by LIMATB laboratory.

The electrical measurements were carried out further to the ASTM D257-99 standard [6] by LAPLACE lab.
The measuring cell used is of the plane-plane type with guard electrode (Fig. 1).

Figure 1. Schematic view of the (A) electrical resistivity measurement and (B) electrical surface resistance measurement



The measurement method used consists of applying a direct voltage U across the terminals of the sample and measuring the current I traversing it after a defined time (1 minute) in order to deduce a resistance R.
The equations for going back to the electrical resistivity thus are as follows:

Eq.3 $$\rho_V = \frac{K_V}{\tau} \times R$$

Eq.4 $$K_V = \pi \frac{(D \times \Phi)^2}{4}$$

Eq.5 $$\rho_V = \frac{2288.1}{\tau\,[mm]} \times \frac{V}{I}$$

With ρ_V : electrical resistivity [Ω.cm] ; $\boldsymbol{\tau}$: average thickness of the shielding material [mm] ; R : electrical resistance [Ω] ; D : 2.125 inch ; $\boldsymbol{\Phi}$: 1 inch ; V : voltage [V] ; I : current intensity measured after 1 minute [A].

Regarding the electrical surface resistance calculation, the following equations were used:

Eq.6 $$\rho_S = \frac{P}{g} \times R$$

Eq.7 $$P = D_0 \times \pi$$

Eq.8 $$\rho_S = 53.4 \times \frac{V}{I}$$

With ρ_S: electrical surface resistance [Ω/□]; g: 0.125 inch; R: electrical resistance [Ω]; D_0: 2.125 inch; V: voltage [V]; I: current intensity measured after 1 minute [A].

The measuring equipment is composed of a Keithley 6517B electrometer as well as a Keithley 8009 test cell. All the measurements were carried out at 100 VDC, the current having been taken up after 1 minute.

All the other characteristics were measured in-house by MAP further to the following ISO standards which are included in the reference section:

- Solids content [7];
- Density using a pycnometer [8];
- Viscosity and pot-life using a RS1 rheometer, Thermofisher [9];
- Hardness [10];
- Tensile stress [11];
- Tear strength [12];
- Young modulus using DMA [13];
- Tg using DSC [14].

3. QUALIFICATION PLAN

In order to qualify the new version of MAPSIL® 214 BV, its characteristics must meet the requirements listed in Tab.2. These requirements come from the characteristics of the current MAPSIL® 214 BV and from the ECSS-Q-ST-70-02C outgassing standard [1].

Table 2. Requirements for MAPSIL® 214 BV silicone resin

Properties	Requirements
Solids content (%)	100
Base/hardener viscosity at 50 s^{-1} (Pa. s)	8 - 12
RML (%)	≤ 1
CVCM (%)	< 0.1

The characterization of the products was performed at the initial state for all the characteristics: rheological, mechanical, outgassing, electrical and thermal properties.
Some of the characteristics were characterized after a damp heat test (7 days at 50°C and 95% RH) and after a cumulative damp heat test + thermal cycling (100 cycles between -170°C and 130°C under N_2 atmosphere).
The polymers used for the formulation of MAPSIL® 214 BV are the same as those used in MAPSIL® 213 and MAPSIL® QS 1123. These polymers have already been evaluated in terms of space uses [15, 16].

4. RESULTS

4.1. INITIAL STATE

4.1.1. GENERAL PROPERTIES

The density of the new version of MAPSIL® 214 BV was measured using a pycnometer further to ISO 2811-1 standard [8]. The value was measured at 1.23. The solids content value was measured according to ISO 3251 standard and is equal to 100%.
The outgassing properties were measured at the Airbus Toulouse facility on a product after 8h curing at 65°C and after one week at normal conditions (23°C and 55% relative hygrometry). The results are listed in Tab.3 [17].

Table 3. Outgassing results for MAPSIL® 214 BV

MAPSIL® 214 BV	TML (%)	RML (%)	CVCM (%)
Current version	0.24	0.23	0.04
New version	0.41	0.35	0.02
New version 1 week at 23°C and 55% RH	0.43	0.38	0.02

4.1.2. RHEOLOGICAL PROPERTIES

The values of the viscosity measurements are listed in Tab.4. The viscosity of the new version of the hardener is close to that of the current one. Regarding the base, a slight increase in the viscosity was observed. Nevertheless, the viscosity of the mix remains close to that of the former one.

Table 4. Viscosity measurements for MAPSIL® 214 BV silicon resin

MAPSIL® 214 BV	Viscosity at 50 s^{-1} (Pa. s) and 23°C		
	Base	Hardener	Mix
Current version	9.3	1.5	8.2
New version	13.4	1.8	9.8

The pot-life was kept at an identical value of 120 minutes at 20°C for the new version of MAPSIL® 214 BV.

4.1.3. MECHANICAL PROPERTIES

For the new version of MAPSIL® 214 BV, hardness was measured following the ISO 7619-1 standard. The value is 52 Shore A whereas it was around 35 for MAPSIL® 214 BV and around 50 for MAPSIL® 214 HV (Table 1).

The tensile strength was measured at 3.5 MPa with an elongation at break of 357%. These measurements were carried out further to the ISO 37 standard.

The tear strength was measured at 5.2 $KN.m^{-1}$ with an elongation at break of 16%. These measurements were carried out further to the ISO 34 standard.

In order to evaluate the adhesion properties of the MAPSIL® 214 BV, lap-shear tests were carried out using PSX and ALU D primers [18, 19] following MAP internal procedure [20] based on NF-EN 1465 standard [21]. 2024-T3 aluminum samples of 1.6 mm thick were used. The average thickness of the adhesive used was 131 ± 7 µm. The tensile-shear strengths were in the range of 2.4 to 3.3 MPa (Table 6) with cohesive type failures for both the current (Fig.2a) and new version (Fig.2b) of MAPSIL® 214 BV. Only one configuration: the current version of MAPSIL® 214 BV samples cured at 65°C for 8 hours using ALU D primer showed some adhesive failures areas (Fig.2c).

The Young modulus was measured using Dynamic Mechanical Analysis (Fig.3). A value of 2.9 MPa was measured for a curing process of 8h at 65°C. When cured at room temperature a value of 2.5 MPa was measured. This slight decrease could be explained by a lower cross-linked polymer network at room temperature. The same observations were made for the current version of MAPSIL® 214 BV: 1 MPa when cured at 65°C during 8 h and 0.8 MPa when cured 7 days at room temperature.

Fig 2. Failure facies of MAPSIL® 214 BV. Cohesive failure for all the samples (a) MAPSIL® 214 BV current version and (b) MAPSIL® 214 BV new version. Adhesive-cohesive failures were observed for only one configuration: (c) current version of MAPSIL® 214 BV samples cured at 65°C for 8 hours using ALU D primer.

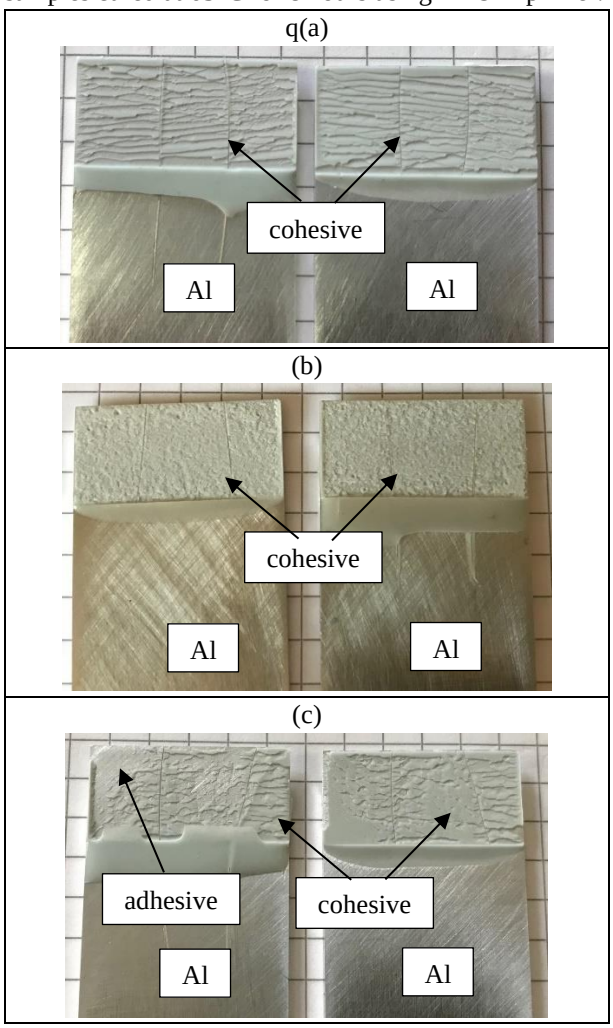
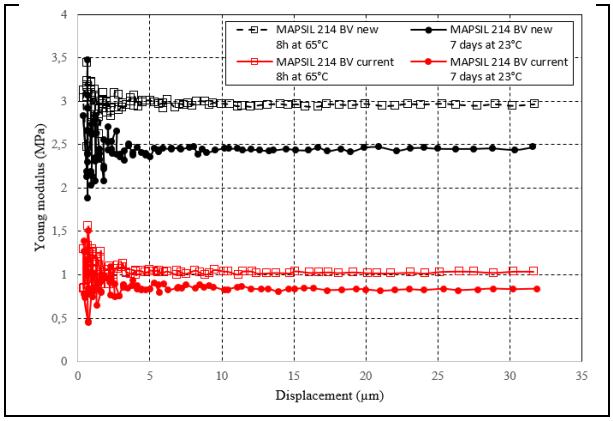


Figure 3. Young modulus at room temperature for MAPSIL® 214 BV current and new versions



The linear coefficient of thermal expansion was measured using TMA. The results are plotted on Figure 4 and in Table 5. A slight increase of CTE was observed for MAPSIL® 214 BV new version but within the same range of the current version.

Figure 4. Linear coefficient of thermal expansion at room temperature for MAPSIL® 214 BV current and new versions

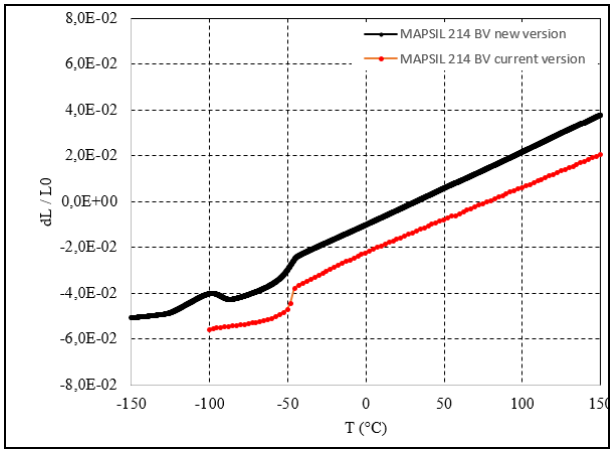


Table 5. Linear coefficient of thermal expansion of the current and the new versions of MAPSIL® 214 BV

	CTE (10^{-6} K^{-1})	
T (°C)	New version	Current version
-40 to 150	318	294

The mechanical properties for current and new versions of MAPSIL® 214 BV are summarized in Table 6.

Table 6. Mechanical properties of the current and the new versions of MAPSIL® 214 BV for both curing conditions: 8h at 65°C and 7 days at 23°C

MAPSIL® 214 BV	New version		Current version	
Curing cycle	8h at 65°C	7 days at 23°C	8h at 65°C	7 days at 23°C
Hardness (ShA)	52	53	33	30
Tensile stress (MPa)	3.9	3.5	2.5	2.8
Elongation at break (%)	300	357	369	512
Tear strength ($kN.m^{-1}$)	4.8	5.2	2.3	2.3
Elongation at break – tearing (%)	13	16	18	26
Tensile-shear stress (MPa) with PSX	2.6	2.6	2.9	3.3
Tensile-shear stress (MPa) with ALU D	2.6	2.5	2.4	2.9
Young modulus	2.9	2.5	1.0	0.8

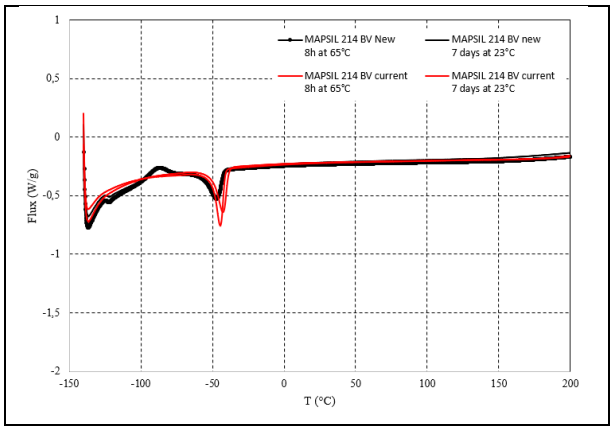
4.1.4. ELECTRICAL PROPERTIES

MAPSIL® 214 BV is an electrical insulating material. The electrical surface resistance was measured to 1.6 x 10^{15} Ω/□. Regarding the electrical resistivity, the value was measured at 5.9 x 10^{16} Ω.cm.
These values are the same as those measured using the current version (Table 1).

4.1.5. THERMAL PROPERTIES

Thermal conductivity was measured further to the flash laser method.
The Cp is 1.37 $kJ.kg^{-1}$. K^{-1} and the density 1.232 $kg.m^{-3}$. The thermal diffusivity was 1.11 x 10^{-7} $mm^2.s^{-1}$.
Using the equation 2, the average thermal diffusivity was 0.19 $W.m^{-1}$. K^{-1} [22].
The DSC measurements were carried out between -150°C and 200°C in order to measure the Tg. The values were close to -123°C for both versions of MAPSIL® 214 BV. These values were confirmed by the TMA analysis used for the CTE measurement.

Figure 5. DSC curve of MAPSIL® 214 BV current and new versions for both curing conditions: 8h at 65°C and 7 days at 23°C



4.2. AFTER AGEING TESTS

Ageing tests were carried out at the CNES facility for the current and the new versions of MAPSIL® 214 BV. A damp heat test was done at 50°C and 95% RH for 7 days. Additional thermal cycling tests were performed under N_2 atmosphere. 100 cycles were performed between -170°C and 130°C with a 10-minute plateau at high and low temperatures (gradient = 5°C/min).
The results are shown in tables 7 to 10.
One may observe a slight increase in the mechanical properties after a damp heat test and after cumulative thermal cycling. This was generally observed for such materials due to post-curing which occurs when submitting the materials at high temperatures.
We may notice that the new version of MAPSIL® 214 BV presents more stable mechanical behavior versus ageing tests. For instance, hardness increases from 52 to 57 for the new version when cured at 65°C for 8 h whereas the hardness increases from 30 to 50 for the current version cured in the same conditions.

Table 7. Mechanical properties at initial state and after ageing tests – New version of MAPSIL® 214 BV cured at 65°C for 8 h

MAPSIL® 214 BV	Initial state	After damp heat test	After damp heat test + Thermal cycling
Hardness (ShA)	52	55	57
Tensile stress (MPa)	3.9	4.1	5.1
Elongation at break (%)	300	262	213
Tear strength ($kN.m^{-1}$)	4.8	4.8	6.5
Elongation at break – tearing (%)	13	13	13
Tensile-shear stress (MPa) with PSX	2.6	2.9	3.3
Tensile-shear stress (MPa) with ALU D	2.6	2.7	3.3

Table 8. Mechanical properties at initial state and after ageing tests – New version of MAPSIL® 214 BV cured at 23°C and 55% RH for 7 days

MAPSIL® 214 BV	Initial state	After damp heat test	After damp heat test + Thermal cycling
Hardness (ShA)	53	53	64
Tensile stress (MPa)	3.5	3.9	5.4
Elongation at break (%)	357	296	213
Tear strength ($kN.m^{-1}$)	5.2	5.1	6.8
Elongation at break – tearing (%)	16	15	12
Tensile-shear stress (MPa) with PSX	2.6	3.0	3.3
Tensile-shear stress (MPa) with ALU D	2.5	2.8	3.4

Table 9. Mechanical properties at initial state and after ageing tests – Current version of MAPSIL® 214 BV cured at 65°C for 8 h

MAPSIL® 214 BV	Initial state	After damp heat test	After damp heat test + Thermal cycling
Hardness (ShA)	33	38	50
Tensile stress (MPa)	2.5	3.4	4.8
Elongation at break (%)	369	425	249
Tear strength ($kN.m^{-1}$)	2.3	2.6	2.7
Elongation at break – tearing (%)	18	17	11
Tensile-shear stress (MPa) with PSX	2.9	3.8	5.3
Tensile-shear stress (MPa) with ALU D	2.4	4.0	5.2

Table 10. Mechanical properties at initial state and after ageing tests – Current version of MAPSIL® 214 BV cured at 23°C and 55% RH for 7 days

MAPSIL® 214 BV	Initial state	After damp heat test	After damp heat test + Thermal cycling
Hardness (ShA)	30	34	50
Tensile stress (MPa)	2.8	2.8	5.0
Elongation at break (%)	512	433	256
Tear strength ($kN.m^{-1}$)	2.3	2.3	-*
Elongation at break – tearing (%)	26	23	-*
Tensile-shear stress (MPa) with PSX	3.3	3.7	5.5
Tensile-shear stress (MPa) with ALU D	2.9	3.9	5.5

*: No value due to sample degradation under thermal cycling

5. CONCLUSION

The current version of MAPSIL® 214 is obtained via a liquid-liquid purification process (patented by CNES), that makes it possible to obtain degassing values compatible with space applications [1]. In order to end the use of organic solvents that do not comply with new European environmental regulations (REACH), the purification process has been modified.

The new version of MAPSIL® 214 BV was characterized at initial state and after ageing tests (damp heat test and cumulative thermal cycling). The characteristics were compared to those of the current version. Except for a slight increase in the mechanical properties at initial state, the general properties remained the same for the new version of the MAPSIL® 214 BV. A more stable mechanical behavior was observed after ageing.

6. ACKNOWLEDGEMENTS

The authors wish to thank P. Nabarra and S. Perraud from CNES for their assistance in carrying out the ageing tests.

7. REFERENCES

1. ECSS-Q-ST-70-02C, Thermal vacuum outgassing test for the screening of space materials, 2008
2. Qualification of adhesives and potting resins produced by MAP, CNES report, 89/CT/DRT/TVE/TH n°074, February 7, 1989;
3. MAP, Technical data sheet – MAPSIL 214
4. ISO 11359-2 standard, Plastics — Thermomechanical analysis (TMA) — Part 2: Determination of coefficient of linear thermal expansion and glass transition temperature, 1999
5. W.I. PARKER, R.J. JENKINS, C.P. BUTLER, G.L. ABBOTT, Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity, Journal of Applied Physics 32, 1961
6. ASTM D257-99 standard, Standard Test Methods for DC Resistance or Conductance of Insulating Materials, 2007
7. ISO 3251 standard, Paints, varnishes and plastics – Determination of non-volatile-matter content, 2008

8. ISO2811-1 standard, Paints and varnishes – Determination of density – Part 1: Pycnometer method, 2011
9. ISO 3219 standard, Plastics – Polymers/resins in the liquid state or as emulsions or dispersions – Determination of viscosity using a rotational viscometer with defined shear rate, 1994
10. NF ISO7619-1 standard, Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 1: Durometer method (Shore hardness), 2006
11. NF ISO 37 standard, Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties, 2012
12. NF ISO 34-1 standard, Rubber, vulcanized or thermoplastic — Determination of tear strength — Part 1: Trouser, angle and crescent test pieces, 2005
13. Dynamic Mechanical analysis – Young modulus measurement, Mettler Toledo technical document,
14. ISO 11357-2, Plastics — Differential scanning calorimetry (DSC) — Part 2: Determination of glass transition temperature, 1999
15. CNES qualification report – MAPSIL QS1123 silicone resin_ DCT/TV/TH/09-14628, 2009
16. CNES qualification report – MAPSIL 213 DCT-TV-TH-2012-13180, 2012
17. Outgassing report, Airbus M19943.6, 2019
18. MAP, Technical data sheet – PSX
19. MAP, Technical data sheet – ALU D
20. MAP Internal procedure for lap-shear bonding, Reference PA026
21. NF EN 1465 standard, Adhesives — Determination of tensile lap-shear strength of bonded assemblies, 2009
22. Measurement of thermal conductivity, LIMATB report, “Rapport MAP_decembre 2019_V1”, 2019