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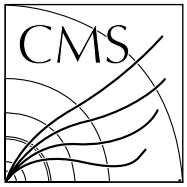

The Compact Muon Solenoid Experiment

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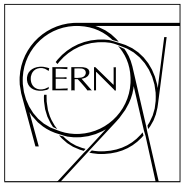

July 17, 2000

Study of some optical glues for the Compact Muon Solenoid at the Large Hadron Collider of CERN

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Abstract

Two Avalanche Photodiodes will measure the light produced in each of the 61,200 PbWO4 crystals composing the barrel part of the electromagnetic calorimeter of the Compact Muon Solenoid (CMS) at the Large Hadron Collider of CERN. To improve the collection of the photons, these detectors will be glued to the crystal. To be used in CMS, the optical glue must fulfil several requirements. The paper describes those requirements and reports the results of the investigation of several commercial optical glues. In particular, refractive index, absorption length, radiation hardness and forecast ageing after 15 years are reported. The most promising glue for CMS was more deeply investigated, in particular its chemical composition, chemical compatibility with the other parts of the calorimeter and curing time in realistic conditions.

1 Introduction

The barrel part of the electromagnetic calorimeter of the Compact Muon Solenoid (CMS) at the Large Hadron Collider of CERN [1] will consist of 61,200 $PbWO_4$ (PWO) crystals. The crystals are cut as pyramid frustum and the light produced in each of them is readout by two Avalanche Photodiodes (APDs), glued to the major base of the crystal. PWO is a negative uniaxial crystal with refractive index close to 2.3 [2] and two main emission bands located at 420 nm (blue) and 520 nm (green) [3]. In recent years, great effort was expended to improve the PWO performance as a scintillator, resulting in significant modification of the crystal properties (radiation hardness, transparency, scintillation spectrum, decay time, etc) [4]; for instance, recently produced crystals exhibit a unique emission band near 430 nm, as shown in Fig.1.

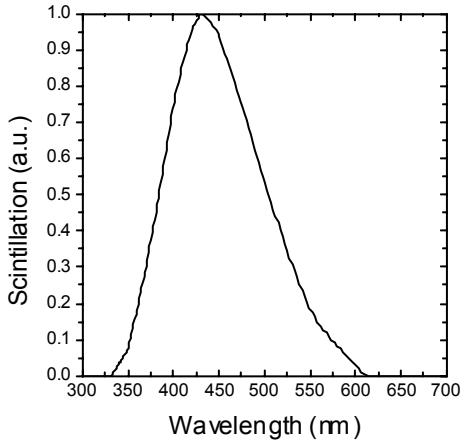


Figure 1: PWO scintillation spectrum expressed as normalised number of emitted photons per unitary interval of wavelength [1].

PWO has a relatively low light yield (about 50 photons/MeV) and its high refractive index limits the amount of photons able to reach the detector, because of internal total reflection [5]. More precisely, the total reflection imposes a cut-off angle on the photons impinging on the major base. This critical angle, $\theta_c = \arcsin(n_{lowest}/n_{PWO})$, depends on the ratio of the lowest refractive index among those of the crossed media, and that of PWO. Therefore to maintain the "detected to emitted" photons (D/E) ratio as high as possible the PWO and the APDs should be coupled with an optical glue having a refractive index not lower than the lowest among those of the materials covering the Si surface of the APDs.

Actually a large variety of optical glues is commercially available. The choice of the best product for CMS has to take into account several requirements, ranging from the efficiency of the optical coupling, to the reliability of the glue curing for the massive use required in the construction of CMS. The present paper reports the main results obtained in investigations of several commercial glues, prompted by the need to select a glue suitable for CMS.

2 Requirements for the glue

To be suitable for CMS the optical glue should fulfil the following requirements:

2.1 Refractive index

Among the APDs considered for CMS, one developed by Hamamatsu has been chosen. From an optical point of view, it is mainly composed of a silicon wafer (Si, $n \sim 4.9$ @ 430 nm), doped along planes parallel to the surface, and coated with a film of silicon nitride (Si_3N_4, $n \sim 2.0$ @ 430 nm), in order to reduce the reflectance of the interface with the silicon. The APD is enclosed in a package and protected with a transparent window [5,6]. Hamamatsu now supplies APDs with an *Epoxy* window with a refractive index of 1.57 at 430 nm replacing the softer *Silicon Resin* used in earlier versions that had an index of 1.47. Thus, in order not to reduce the number of

photons reaching the diode, the refractive index of the glue coupling the PWO and the APDs should be at least as high as that of *Epoxy* in the wavelength range of the PWO scintillation spectrum, 330-615 nm (Fig. 1).

2.2 Absorption length

In the first version of the *Epoxy* protected APDs, the centre of the window was about 0.3 mm depressed with respect to the package border. Hamamatsu now produces APDs with a flat or slightly convex window surface, but 0.3 mm can be considered as an upper limit of the glue layer thickness in the PWO-APD system. The glue layer does not reduce the light collection if the absorption length, $\alpha^{-1} = \left(4\pi k/\lambda\right)^{-1}$, with k the extinction coefficient and λ the wavelength, is much greater than the layer thickness in the wavelength range of the PWO scintillation spectrum.

2.3 Mechanical adhesion

In the final assembly the APDs will be mounted, in pairs, in capsules equipped with a kapton cable and a connector for the electrical contacts. The capsule is designed to fit the major base of the PWO crystal and ensure the co-planarity of the APD and the crystal surfaces during the gluing operation. The optical glue should provide both the optical matching between the PWO and the APDs, and the mechanical adhesion between the PWO and the capsule. The mechanical adhesion was simply tested by trying to manually remove the capsule 24 hours after the gluing.

2.4 Curing time

According to the CMS construction schedule, at the two Regional Centres of CERN and Rome, every day about 30 crystals should have capsules glued on to them. The gluing operation will be done on dedicated benches, equipped with instruments for quality control [7]. After 24 hours, the glue should be enough cured to allow the removal of PWO-capsule units from the benches.

2.5 Chemical compatibility

The glue must not be dangerous for the neighbouring components: PWO, APD, capsule, kapton and alveolar structure housing the crystals.

2.6 Ageing and Radiation Hardness

The glue properties should not degrade during the CMS lifetime (about 15 years: 5 of construction plus 10 of running). The effect of natural ageing can be predicted by the accelerated ageing induced by heating glue specimens at several temperatures higher than the CMS operating temperature (about 18 °C), assuming a relationship between damage and temperature [8]; in particular we assume the Arrhenius model

$$t = C \exp\{E_a / KT\} \tag{1a}$$

where t is the time to reach a specified endpoint or lifetime at the temperature T [K], E_a is the activation energy [eV], K the Boltzman constant [eV/K] and C a constant depending on the material. If t_1 and t_2 are the times elapsing to observe the same damage when the specimen is exposed, respectively, at the temperatures T_1 and T_2, the coefficient C and the activation energy E_a are given by

$$\begin{cases} C = t_1 \exp\{-E_a / KT_1\} \\ \dfrac{E_a}{K} = \ln\left(\dfrac{t_1}{t_2}\right) \Big/ \left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) \end{cases} \tag{1b}$$

With respect to the working temperature T_0, the acceleration factor a of the ageing at the temperature T_j is

$$a = \exp\left\{\frac{E_a}{K}\left(\frac{1}{T_0} - \frac{1}{T_j}\right)\right\}. \tag{1c}$$

Here and in the following, “damage” refers to the reduction of the glue absorption length; the absorption length has to be measured before and after each accelerated ageing test. The thermal ageing tests were accomplished with the climatic chambers of INN/TEC at ENEA-Casaccia, Rome and at PSI, Villigen.

The glue degradation is not only due to the normal ageing occurring at room temperature (RT), but also to the hostile environment of CMS: by the end of the CMS lifetime the glue layer will have been irradiated, mainly with slow (ca 1 MeV) neutrons with a fluence of 2 10^{13}/cm^2, and with lower doses of other hadrons and electromagnetic particles [9]. The radiation hardness tests consisted in the separate irradiations of glue specimens with neutrons with the expected integrated doses, and with gammas and 70 MeV protons with equivalent integrated doses. The irradiation tests were carried out at the *Calliope* and *Tapiro* plants (ENEA-Casaccia) and at PSI.

It should be noted that the separate study of normal ageing and radiation hardness is not completely realistic because it does not consider the effect due to the superposition of different processes (i.e. from radiation and natural ageing). However a facility allowing more realistic tests is not available.

3 Glue optical characterisation

3.1 Method

The complex refractive index of the glue is determined starting from the transmittance T and reflectance R spectra, measured at (near) normal incidence. The measurements were accomplished with a Lambda 19 spectrophotometer in the wavelength range 300-700 nm that completely covers the PWO scintillation spectrum (see Fig.1). For both measurements, the spectrophotometer was equipped with a 15 cm integrating sphere in order to avoid errors due to poor flatness and parallelism of the glue layer interfaces.

The specimens were obtained by filling with glue a special container, consisting of a fused silica substrate (3mm thick, 25mm diameter) sealed to an aluminium o-ring (1 mm thick, 25mm external diameter, 20 mm internal diameter) with a small amount of a cyanoacrylate adhesive positioned along the external perimeter. The curing procedure indicated by the manufacturer was then followed. The final thickness of the cured glue layer was measured with an optical microscope, where the focussing was adjusted with a micrometer, by comparing the focus position of the glue//air interface with those of the o-ring.

First of all, the complex refractive index of the substrate, n_s-ik_s, was numerically determined at several wavelengths by minimising the merit function

$$MF\left(\lambda, n_s, k_s\right) = \frac{1}{2}\left\{\left(\frac{T_{EXP}\left(\lambda\right) - T_{CAL}\left(\lambda, n_s, k_s\right)}{\Delta T}\right)^2 + \left(\frac{R_{EXP}\left(\lambda\right) - R_{CAL}\left(\lambda, n_s, k_s\right)}{\Delta R}\right)^2\right\} \qquad (2)$$

where ΔT (about 0.2%) and ΔR (about 0.1%) are the experimental errors; the subscripts stand for experimental and calculated quantities; the equations describing the T and R spectra of a material slab are reported in [10]. In the minimum $MF < 1$ and the width of the neighbouring region where $MF \leq 1$ gives the error on the determined complex refractive index.

Once the substrate is characterised, the complex refractive index of the glue can be determined in a similar way; this time the equation describing the T and R spectra are obtained by the recursive application of the formula reported in [10].

As a general rule, n is most sensitive to R, and k to T.

3.2 Results

The commercial glues investigated in the present work are listed in Table 1; the glues are ordered according to the curing condition, ranging from simple solvent evaporation (*Histomount*) to heating in a controlled atmosphere (*Epoxy*). The latter is considered here because it is the material composing the protective window of the APDs to be used, but its curing condition is too complex to be adopted for CMS.

Table 1: investigated glues

(rtv stands for room temperature vulcanising)

product	**Manufacturer**	**Components**	**curing**
Histomount	National Diagnostic	One	12 h @ RT (solvent evaporation)
rtv 3145	Dow Corning	One	3 days @ RT (reacts with air moisture)
NOA 61	Norland Optical Adhesive	One	10 min with UV (350-380nm) 5mW/cm^2
UVO114	Epotek	One	1-2min with UV (300-400nm) 100mW/cm^2
Melmount 1.582	Cargille	One	(thermoplastic) liquid @ 70°C
Melmount 1.704	Cargille	One	(thermoplastic) liquid @ 70°C
Naphrax	Northern Biological Supplies Ltd	One	(thermoplastic) liquid @ 70°C
TSE 3250	GE Bayer Silicones	One	4 h @ 100°C
rtv 615	GE Bayer Silicones	Two	pot life: 4 h 6-7 days @ 25°C 4 h @ 65°C
rtv 301	Epotek	Two	pot life: 1 h 1 day @ RT
rtv 301-2	Epotek	Two	pot life: 8 h 2 days@ RT
rtv 302	Epotek	Two	pot life: 5-10 min 1 h @ RT
X-38-406	Shin Etsu	Two	pot life: 8 h 4 h @ 100°C
Epoxy	Shin Etsu	Two	150°C in nitrogen

Several specimens of each glue were prepared, measured and characterised according to the methods described above. As an example, figure 2 shows the *T* and *R* spectra of the bare fused silica substrate and the *Histomount* specimen.

Figure 3 shows the refractive index and the extinction coefficient, expressed in terms of the absorption length, as calculated at several wavelengths by means of the minimisation of the merit function. The sensitivity range of the spectrophotometer and the experimental errors did not allow the determination of absorption lengths

larger than some ten centimetres or shorter about 0.1 mm for a glue layer 1mm thick. But investigation outside this range is not needed to evaluate the effectiveness of the glue for CMS.

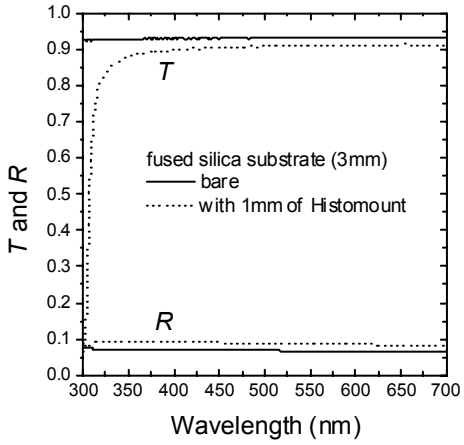
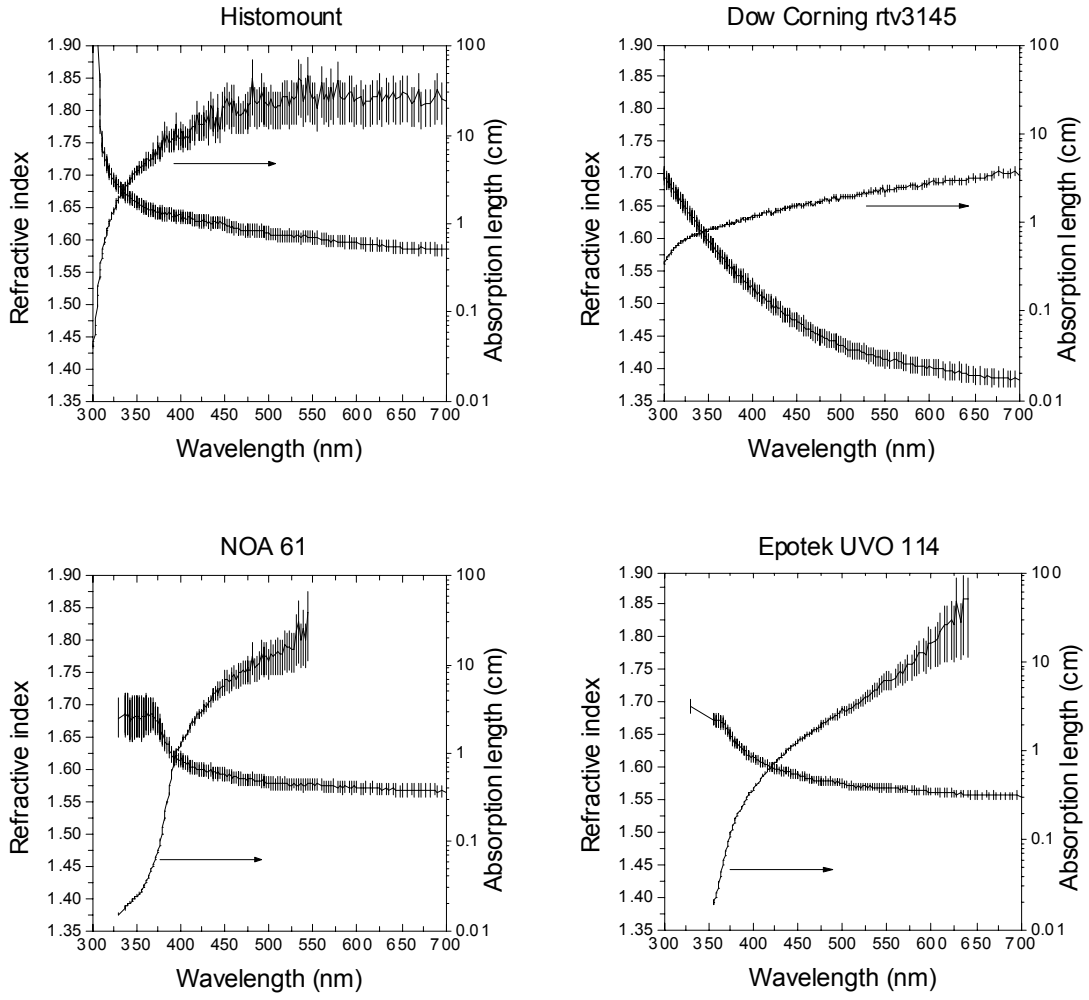
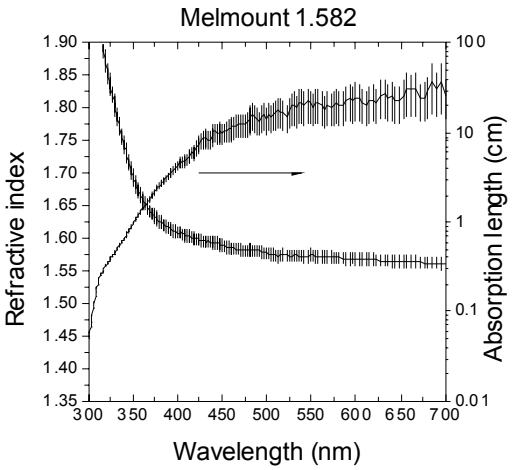
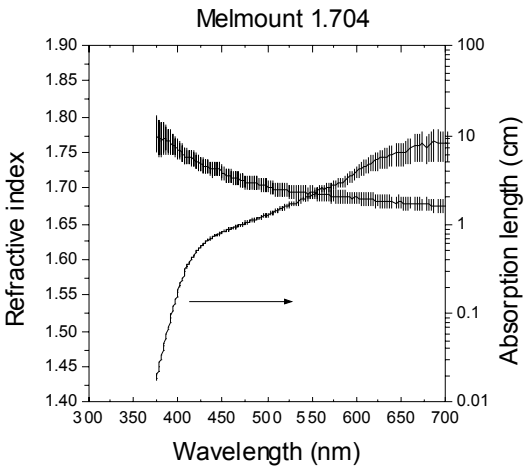
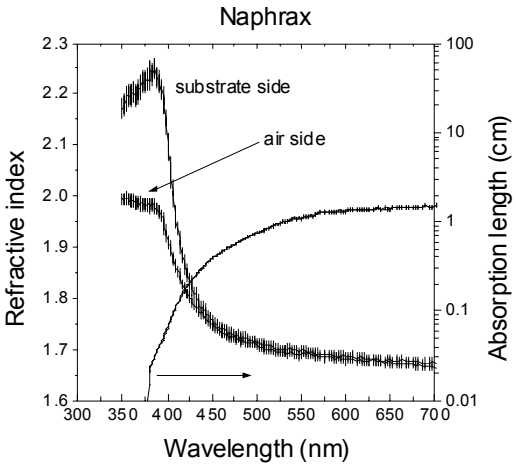


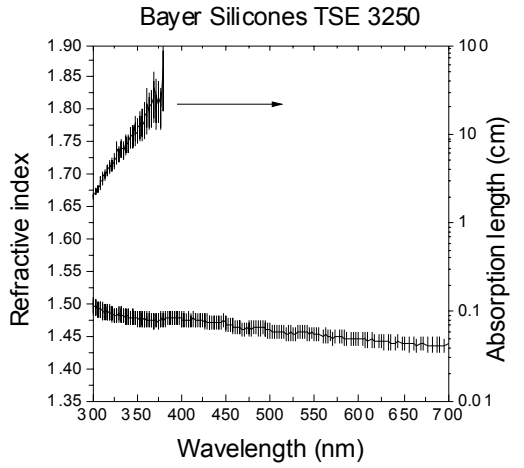
Figure 2: transmittance and reflectance spectra of the bare fused silica substrate (SiO_2) and of the *Histomount* specimen, Histomount(1mm)// SiO_2(3mm)

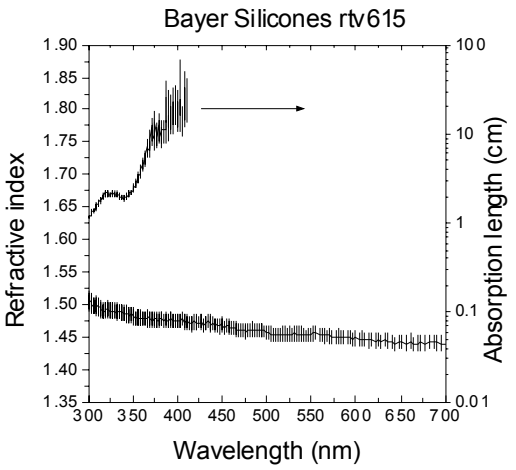


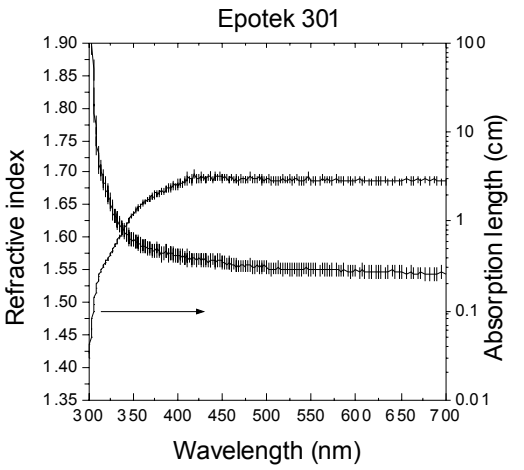

Melmount 1.582
Refractive index
Absorption length (cm)
Wavelength (nm)


Melmount 1.704
Refractive index
Absorption length (cm)
Wavelength (nm)


Naphrax
substrate side
air side
Refractive index
Absorption length (cm)
Wavelength (nm)


Bayer Silicones TSE 3250
Refractive index
Absorption length (cm)
Wavelength (nm)


Bayer Silicones rtv615
Refractive index
Absorption length (cm)
Wavelength (nm)


Epotek 301
Refractive index
Absorption length (cm)
Wavelength (nm)

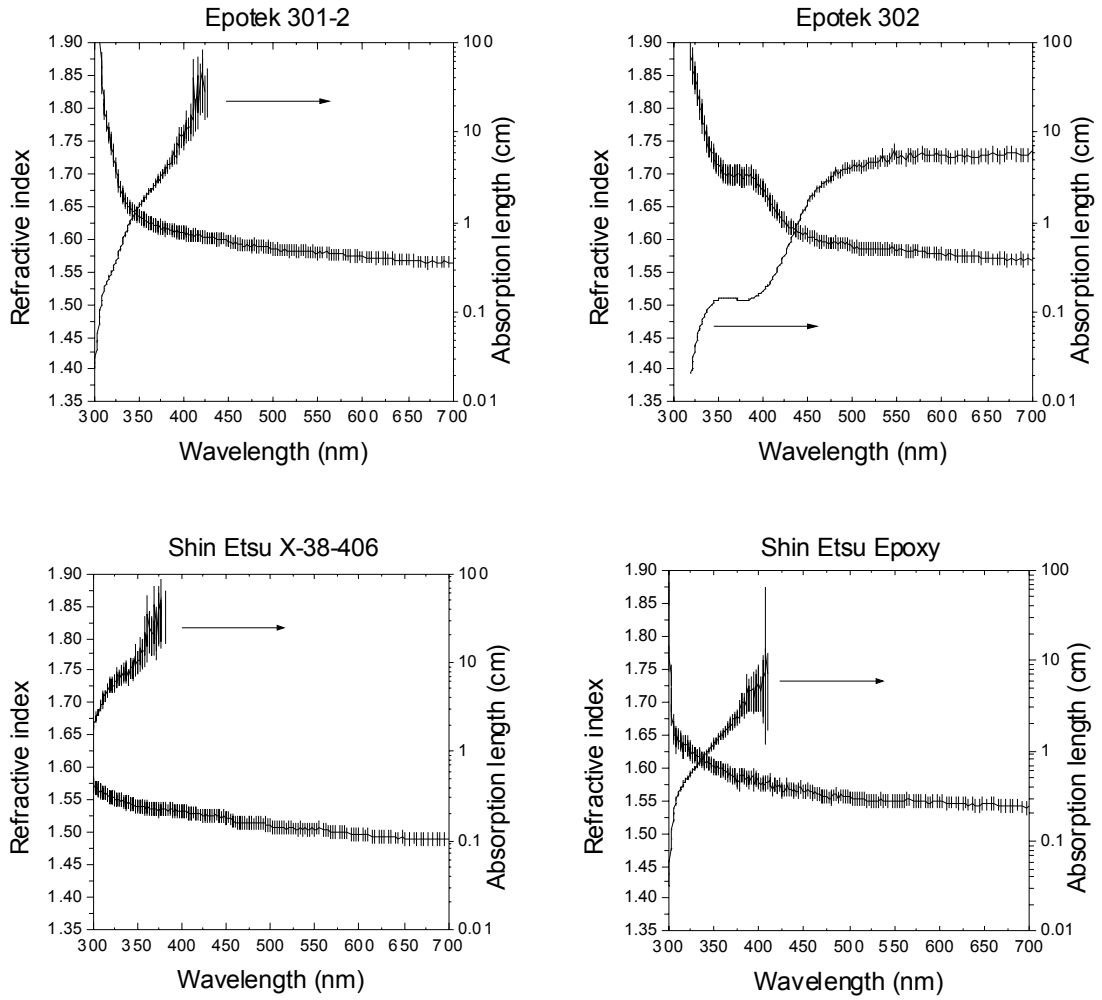


Figure 3: refractive index and absorption length of the investigated glues as determined from the spectrophotometric measurements in the 300-700 nm range.

Among the investigated glues, *Naphrax* shows the strangest behaviour: moving towards the UV, the transmittance drastically decreases at about 380 nm, but never equals zero, remaining about 2-3% till 300 nm. In general, materials whose transmittance is cut-off towards shorter wavelength, like glass, ZnSe, PWO, etc., never show such a plateau below the cut-off wavelength. Further investigation clarified that the anomalous behaviour is due to luminescence: Fig. 4 compares the spectrum measured with the Perkin Elmer spectrophotometer with the experimental data obtained with an ad hoc set-up where the luminescence is suppressed by monochromatising the measurement beam twice, before and after the sample. According to the new data, the Naphrax transmittance is zero below 380 nm and luminescence appreciably affects the transmitted beam below 400 nm, where a shoulder is visible in the spectrum profile. Unfortunately, due to the poor signal to noise ratio, the ad hoc set-up did not allow the evaluation of the influence of the luminescence on the reflectance spectrum. The use of the reflectance air-side or substrate-side spectra for the refractive index determination, leads to different evaluations below 400 nm; this strange behaviour is probably also due to luminescence.

Even if much less marked, the transmittance spectra of the two UV curing glues seem to be affected by luminescence, showing a plateau of about 0.5% under the cut-off wavelength. For these glues the optical characterisation is performed above the cut-off wavelength range and the complex refractive index at 330 nm (the inferior limit of the PWO scintillation spectrum) is calculated by linear extrapolation from the data of the cut-off region.

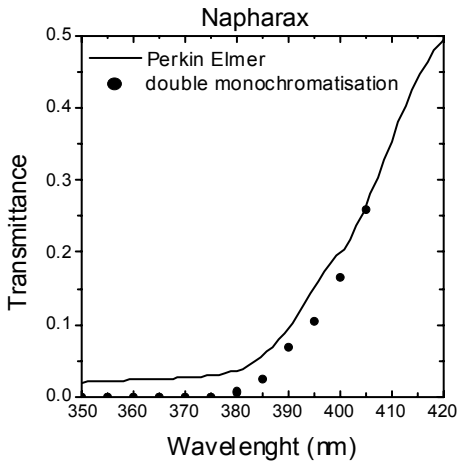


Figure 4: transmittance measured with a Perkin Elmer spectrophotometer, equipped with an integrating sphere, compared with the results obtained with an ad hoc set-up where the measurement beam is monochromatised twice, before and after the specimen.

Table 2 summarises the results of the optical characterisation reporting: i) the refractive index at 430 nm, where the PWO scintillation is maximum; ii) the absorption length averaged over the PWO scintillation spectrum <Λ>; iii) the ratio detected to emitted photons (D/E) averaged over the PWO scintillation spectrum and the incident angle and the polarisations, *s* and *p*, calculated by

$$\frac{D}{E}=\frac{1}{2}\frac{\int_0^{\pi/2} d\theta \int_{330}^{615} d\lambda \ \frac{1}{2}\left[T_p(\lambda,\theta)+T_s(\lambda,\theta)\right]\mathrm{IQE}(\lambda)S(\lambda)}{\int_{330}^{615} d\lambda \ S(\lambda)} \tag{3}$$

where: a) $T_p(\lambda,\theta)$ and $T_s(\lambda,\theta)$ are the calculated transmittances from PWO to Si of the APD at the incidence angle θ (in PWO) [5] for, respectively, *p* and *s* polarisation; b) $S(\lambda)$ is the PWO scintillation spectrum expressed as emitted-photon number for unitary interval of wavelength; c) IQE(λ) is the "intrinsic" detector quantum efficiency, that is the quantum efficiency for the photons that have reached the Silicon wafer after the crossing of the protective window and the antireflective layer. For simplicity here the intrinsic quantum efficient was considered unitary in the whole scintillation range, PWO and Si as semi-infinite media, and the interposed layers infinitely extended. The thickness of the Si_3N_4antireflective coating affects the ratio D/E and its optimal value depends on the considered glue, by way of its refractive index. As an example Fig.5 shows D/E versus the Si_3N_4 thickness for the Cargille products and Naphrax, which refractive indices are representative of the considered products. Because D/E does not dramatically depend on the thickness, in the following the APDs are assumed to be coated with 65 nm of Si_3N_4 in all the cases.

To determine the glue's effectiveness as a coupling medium, the ratio D/E is first calculated considering the APD without the protective window, i.e. the system PWO//glue//Si_3N_4(65nm)//Si. The comparison between the values obtained with the glue layer 0.3 mm and 1 mm thick, respectively reported in the 4th and 5th columns, gives an idea of the role of the glue's absorption. Finally, the last column reports D/E for the system PWO//glue(0.3mm)//*Epoxy*(0.3mm)//Si_3N_4(65nm)//Si; in this case, because of the presence of the window, there is no great advantage in using glue with a refractive index higher than that of the *Epoxy*.

The absorption lengths of the Cargille products (*Melmount 1.704* and *1.582*) and of *Naphrax* are in good agreement with the previous measurements of T. Kirn et al. [11].

On the basis of the results of the optical characterisation, we ended the investigation of the glues less suitable for CMS. Relative to *NOA61*, *UVO114* has a shorter absorption length and the curing requires much more UV power; this prevents its use in CMS because of UV radiation damage to the PWO [12]. We verified that the UV dose required for the curing of *NOA61* reduces by about 1% the longitudinal transmittance of full size crystals and after a few days the observed damage is totally recovered without any special care. Among the Epotek rtv products, *rtv302* is the least satisfactory because of the short absorption length.

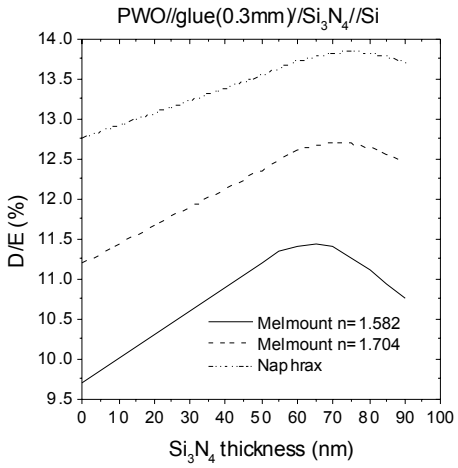


Fig 5: D/E versus the Si_3N_4 thickness for some glues; the APD has no protective window

Table 2: main optical characteristics of the investigated glues (see text)

product	***n* @ 430 nm ± 0.01**	**<Λ> (cm)**	**D/E (0.3 mm) (%)**	**D/E (1 mm) (%)**	**D/E (0.3 mm) epoxy window (%)**
Histomount	1.63	> 10	12.0	12.0	11.2
rtv 3145	1.49	1.44 ± 0.06	9.4	9.1	9.4
NOA 61	1.59	0.55 ± 0.01	11.3	10.9	10.9
UVO114	1.60	0.371 ± 0.009	11.0	10.4	10.7
Melmount 1.582	1.60	6.8 ± 1.5	11.4	11.4	11.1
Melmount 1.704	1.73	0.10 ± 0.01	12.8	11.6	10.3
Naphrax	1.80	0.086 ± 0.003	13.8	11.1	9.7
TSE 3250	1.47	> 30	9.4	9.4	9.4
rtv 615	1.47	> 15	9.4	9.4	9.4
rtv 301	1.57	2.8 ± 0.3	10.9	10.7	10.9
rtv 301-2	1.60	> 10	11.5	11.5	11.1
rtv 302	1.62	0.466 ± 0.009	11.5	10.6	10.8
X-38-406	1.53	> 25	10.3	10.3	10.3
Epoxy	1.57	12 ± 6	10.9	10.9	10.9

4 Accelerated ageing tests

The glue specimens together with a bare substrate were measured and characterised after each ageing test. Repeating the substrate characterisation after each test makes the glue characterisation free from the effects of any ageing of the substrate itself. We observed that the glue refractive index is unchanged after the ageing tests. For this reason in the following the effect of the ageing is represented in terms of the glue absorption length only.

The results of accelerated ageing tests on the Cargille products (*Melmount 1.704* and *1.582*) and *Naphrax* can be found in [11].

4.1 Irradiation

Table 3 summarises the results of the irradiations of the glue specimens. In particular the last column reports D/E calculated using the shortest absorption length determined after irradiation, and considering the APD without protective window and a glue layer 0.3 mm thick; the corresponding value before the irradiation is reported in the 4th column of Table 2. The Epotek glues, *rtv 301* and *301-2* are not sufficiently radiation hard for CMS because the absorption length is substantially reduced to be not much greater than the thickness of the glue layer (0.03 cm) with a consequent reduction of the ratio D/E. *Histomount*, *X-38-406* and *Epoxy* are more sensitive to proton irradiation, *rtv3145* to gammas, but they can be considered radiation hard for CMS. *NOA61, TSE3250* and *rtv615* are substantially unaffected by any irradiation.

Table 3: results of the irradiation tests; <Λ> is the absorption length averaged over the PWO scintillation spectrum; D/E is the ratio "detected to emitted" calculated from Equation (3) for an APD without *Epoxy* window by using the shortest absorption length observed after the irradiations.

	<Λ> (cm)				**Worst D/E** (0.3mm) (%)
Product	**Initial**	**Gamma** 4000 Gy	**Neutron** 2 10^{13} n/cm^2	**Proton** 2 10^{13} p/cm^2	
Histomount	> 10	12 ± 3	> 10	8 ± 2	12.0
Rtv 3145	1.44 ± 0.06	0.79 ± 0.02	1.47 ± 0.06	1.29 ± 0.06	9.3
NOA 61	0.55 ± 0.01	0.55 ± 0.01	0.55 ± 0.01	0.55 ± 0.01	11.3
TSE 3250	> 30	> 20	> 30	> 30	9.4
rtv 615	> 15	> 15	> 15	> 15	9.4
rtv 301	2.8 ± 0.3	0.139 ± 0.001	/	/	9.5
rtv 301-2	> 10	0.166 ± 0.001	/	/	10.3
X-38-406	> 25	> 15	> 20	3.2 ± 0.3	10.3
Epoxy	12 ± 6	8 ± 3	12 ± 6	3.1 ± 0.4	10.9

4.2 Thermal accelerated ageing

TSE3250 and *X-38-406* were not further investigated because for them the PWO//APD gluing tests gave negative results: probably due to the glue shrinking, after cooling most of the APD surface was disconnected from the glue, leaving an air gap.

The thermal accelerated ageing test consisted of heating two separate specimens, two for each glue, at 80 (353) and 110 (383) ºC (K). The specimens were optically characterised before and after several steps of heating. In the single heating step, the rate of the initial and final temperature transients (RT ↔ 80 or 110 ºC), was 1 ºC/minute; during the test the temperature was maintained constant. A continuous temperature cycling was

not adopted, because in CMS the temperature will be kept almost constant, at 18 ºC (291 K). For similar reasons, the humidity was not raised to high values.

Figure 6 shows the modification induced by heating on transmittance and the extinction coefficient (k) of *Histomount, rtv3145, NOA61, rtv615* and *Epoxy* after periods when the difference from the initial condition is evident enough. To make easier the quantitative study of ageing after different periods of heating, the $k(\lambda)$ spectra of each glue were fitted with suitable empirical functions, given below (4a – 4e). The parameters A and B were determined by the fits.

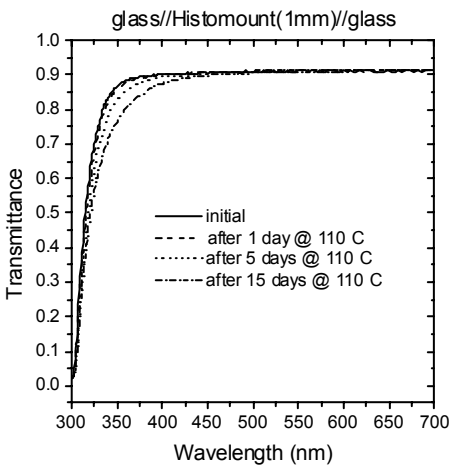
$$\textit{Histomount}:\ k(\lambda) = 17.6\cdot 10^{-5}\exp\left\{-(\lambda-290)^2/11^2\right\} + A\cdot 10^{-5}\exp\left\{-(\lambda-138)^2/115^2\right\} \tag{4a}$$

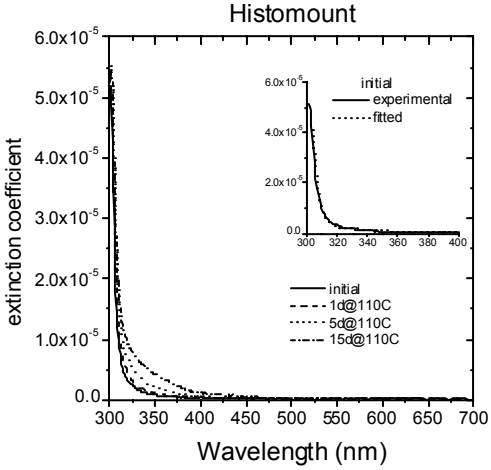
$$\textit{rtv 3145}:\ k(\lambda) = A\cdot 10^{-5}\exp\left\{-(\lambda-165)/41\right\} + 4.3\cdot 10^{-5}\exp\left\{-\lambda/120\right\} + 1.4\cdot 10^{-6} \tag{4b}$$

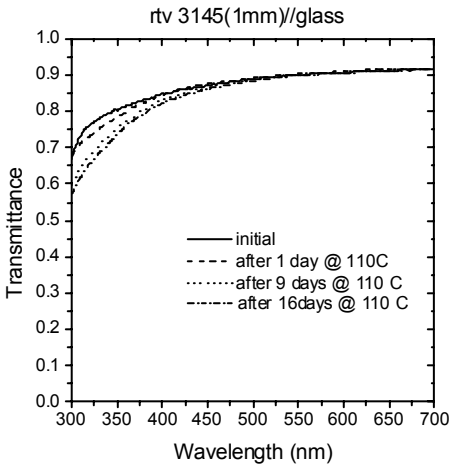
$$\textit{NOA61}:\ k(\lambda) = \frac{A\cdot 10^{-4}}{1+(\lambda/366)} + 4.88\cdot 10^{-7}\exp\left\{B(454-\lambda)\right\} \tag{4c}$$

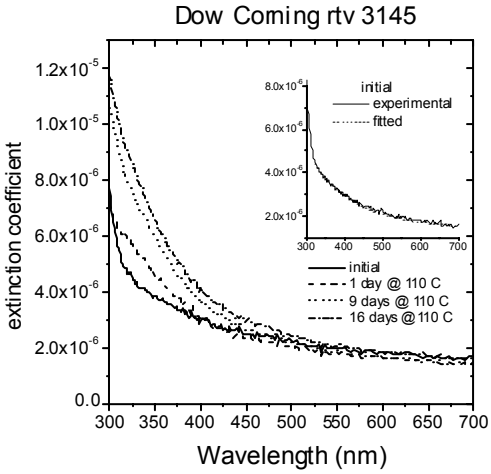
$$\textit{rtv615}:\ k(\lambda) = A\cdot 10^{-5}\exp\left\{-\lambda/30.5\right\} - 9\cdot 10^{-8} \tag{4d}$$

$$\textit{Epoxy}:\ k(\lambda) = A\cdot 10^{-5}\exp\left\{-(\lambda-310)/34.5\right\} \tag{4e}$$









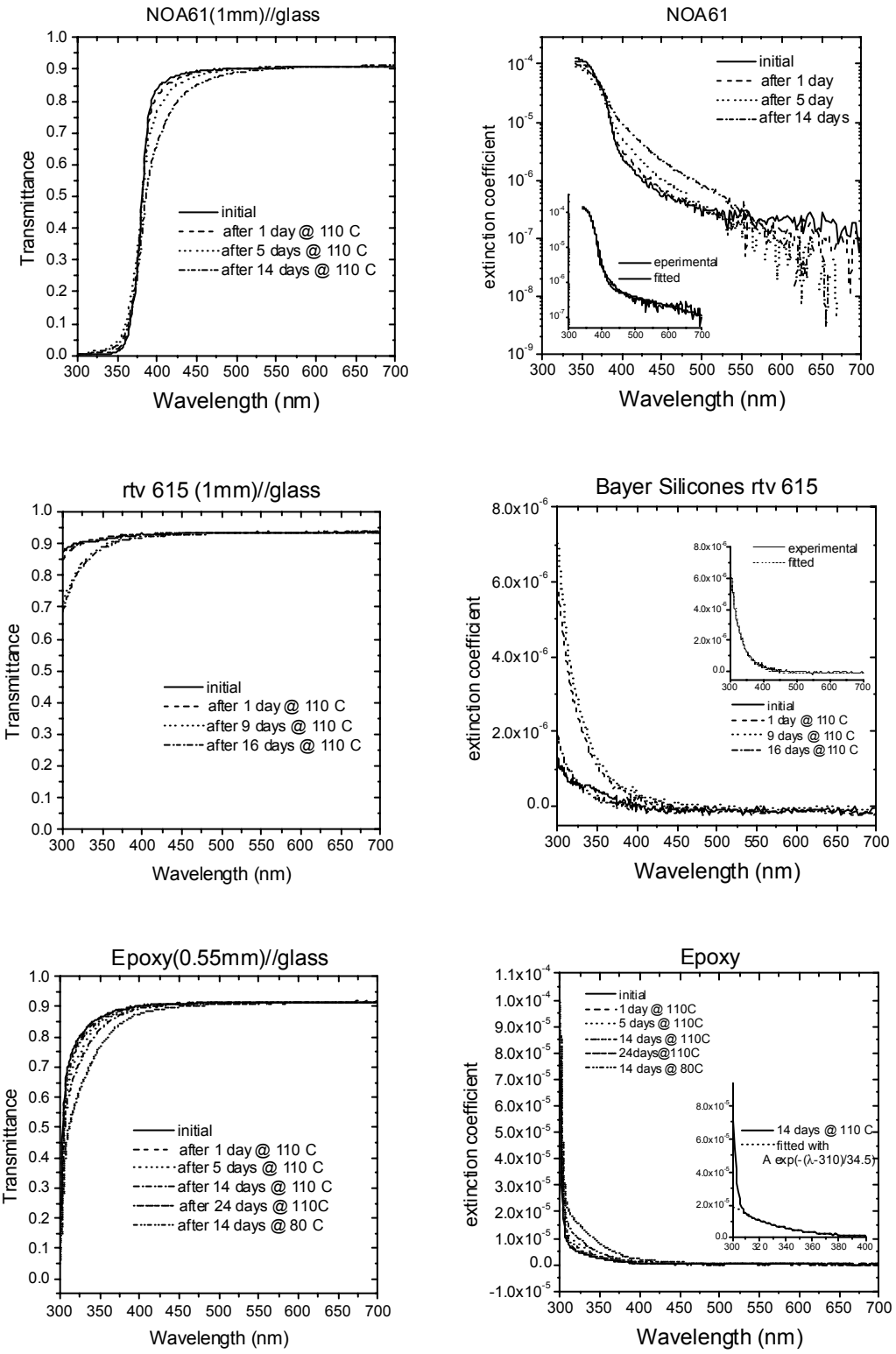
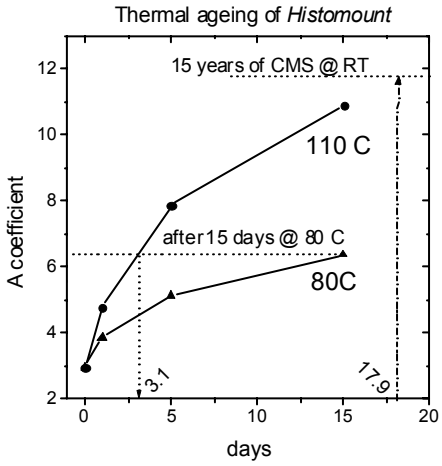
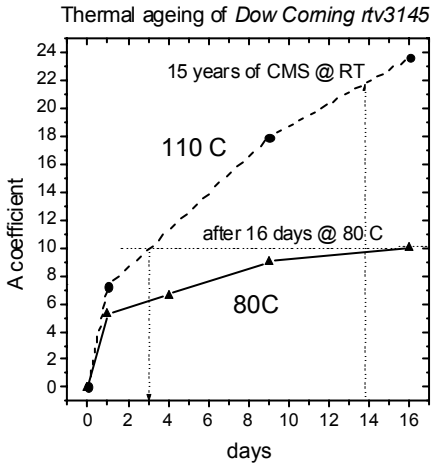
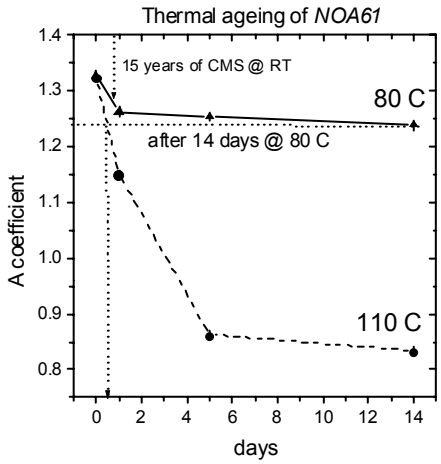
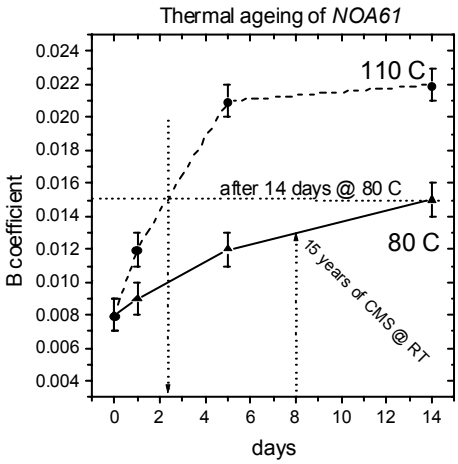


Figure 6: transmittance and extinction coefficients of the glues before and after several periods at 80 and 110 ºC.


Thermal ageing of *Histomount*
15 years of CMS @ RT
110 C
after 15 days @ 80 C
80C
3.1
17.9
A coefficient
days


Thermal ageing of *Dow Corning rtv3145*
15 years of CMS @ RT
110 C
after 16 days @ 80 C
80C
A coefficient
days


Thermal ageing of *NOA61*
15 years of CMS @ RT
80 C
after 14 days @ 80 C
110 C
A coefficient
days


Thermal ageing of *NOA61*
110 C
after 14 days @ 80 C
80 C
15 years of CMS @ RT
B coefficient
days

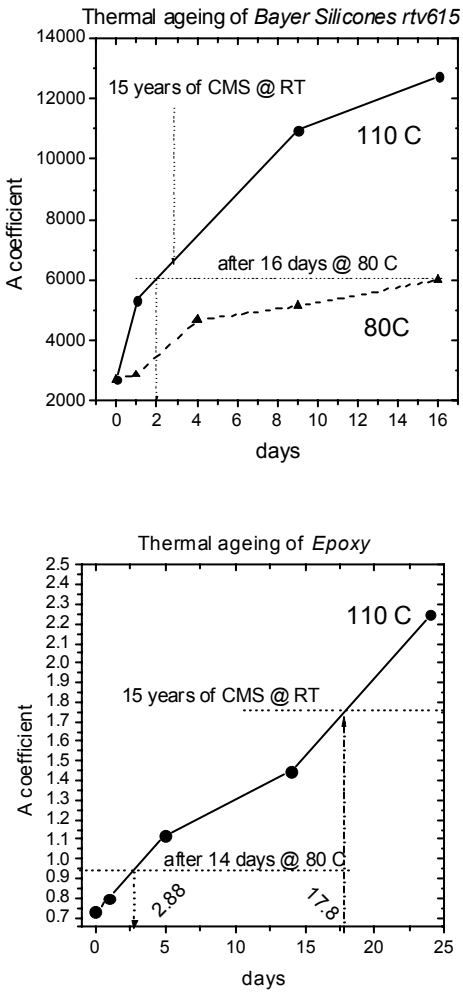


Figure 7: best fit parameters of $k(\lambda)$ measured before and after several thermal ageing periods.

Figure 7 shows the behaviour of the fitting parameters versus the total time of the exposure to 80 and 110 ºC. In all cases the effects induced at 110 ºC are larger than those induced at 80 ºC.

Under the hypothesis that Arrhenius' law governs the thermally induced damage, the degradation after 15 years at RT can be deduced by the damage observed at higher temperature. In particular the activation energy E_a was calculated with Equations 1b by the exposure times at 110 and 80 °C giving the same damage and reported in Figure 7. Then the acceleration factor was calculated with Equation 1c allowing the prediction of the damage after 15 years. Table 4 summarises the results of the data analysis and reports the damage expected after 15 years at RT in terms of the absorption length, averaged over the PWO scintillation spectrum, and of the ratio D/E. According with the thermal accelerated ageing test, at RT all the examined glues degrade during 15 years insufficiently to reduce the performance of the CMS calorimeter.

In conclusion, taking into account the curing conditions, the results of the optical characterisation and the accelerated ageing and irradiation tests, *Histomount* seems to be the best candidate to glue PWO crystals and capsules in CMS. But before the final acceptance of *Histomount*, two very important points had to be investigated: the mechanical adhesion of the PWO//capsule and the chemical compatibility with the neighbouring components.

Table 4: results of the thermal accelerated ageing tests. E_a is the activation energy; a is the acceleration factor relative to ageing at RT; <Λ> is the absorption length averaged over the PWO scintillation spectrum; D/E is the ratio "detected to emitted" photons, Equation (3), for an APD without *Epoxy* window

Product	E_a/K (°K)	a	**after 15 years @ RT**		
			fit parameters	**<Λ> (cm)**	**D/E (0.3mm) (%)**
Histomount	7120	302 @ 110 ºC	A = 11.8	3.6 ± 0.5	11.9
rtv 3145	7440	390 @ 110 ºC	A = 21.6	1.36 ± 0.09	9.4
NOA61	A:15000 B: 8140	A: 6072 @ 80 ºC B: 684 @ 110 ºC	A = 1.269 B = 0.013	0.56 ± 0.01	11.3
rtv 615	9371	1836 @ 110 ºC	A = 6580	> 15	9.4
Epoxy	7126	303 @ 110 ºC	A = 1.76	4.8 ± 1.4	10.9

5 Further investigation of *Histomount*

5.1 Chemical composition

The results of the chemical analysis carried out at the Chemical Division of ENEA-Casaccia indicate that *Histomount* consists of vinyl toluene and a mixture of meta-, para- and ortho-xylene. The xylene inhibits the polymerisation of the vinyl toluene, which then occurs as the xylene evaporates. Even though the content of xylene in *Histomount* is quite low its toxicity will require precautionary measures in mass production.

5.2 Compatibility of *Histomount*

The compatibility of *Histomount* with the diode itself and with neighbouring components was tested in quite drastic conditions to accelerate the effects. The electrical characteristics, in particular the operating voltage for a gain of 50, breakdown voltage and dark current of APDs were measured before being brought into contact with Histomount or xylene. An APD without any (*Epoxy)* protective coating over the silicon nitride was then glued onto a glass substrate and placed at a temperature of 80 ºC for 3 weeks. The electrical properties were then remeasured and found to be unchanged. This APD was then given the full standard irradition with protons and its properties again measured: the operating voltage for gain 50 was unchanged, the breakdown voltage was reduced by 2 volts, typical for that type of APD, and its dark current, 3.7 microamps, was also similar to that of other irradiated APDs. Since the xylene largely evaporates in the gluing process, APDs were also immersed in pure xylene: An APD coated in *Epoxy*, and an APD with no protective coating were immersed in xylene for 2 months and their electrical properties found to be unchanged. The Epoxy was observed to be slightly softened, but this does not appear to have any serious consequences,. (On the other hand the silicon resin earlier used to coat the APDs was damaged, leading to destruction of the electrical contact on the diode, in less than a day.)

A piece of the material constituting the capsule was kept immersed in xylene for one month and no effect was observed.

The kapton cable with connector used in the capsule and a piece of the reflective wrapping used in the alveolar structure, were kept in saturated xylene vapour in a sealed bottle. After one month the kapton and the reflectance of the wrapping were unmodified; the plastic package of the connector of the kapton was bent, but without consequence for the electric contacts.

We have found no evidence of incompatibility between *Histomount* and each of the first neighbourhood components.

5.3 Monitoring of the curing in realistic conditions

The curing time is an important characteristic that must be taken into account for the choice for CMS. *Histomount* cures by the evaporation of the solvent, xylene, whose refractive index (about 1.5) is lower than that of vinyl toluene. For this reason, the refractive index of *Histomount* rises as the content of xylene falls. Thus measuring the refractive index provides a monitor of the *Histomount* curing.

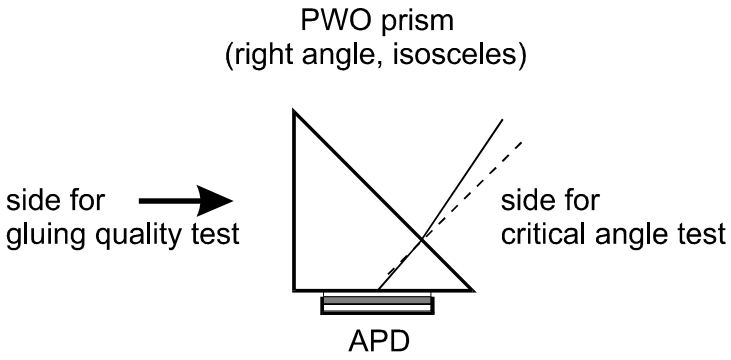


Figure 8: monitoring of the gluing with PWO prism

Figure 8 shows a very simple way to monitor the curing in the condition of use in CMS. The APD, or the capsule, is glued on one of the two cathetus-sides of a PWO-right-angle-isosceles prism. The gluing quality can be checked with the tools proposed in [7] by viewing the APD from the other cathetus-sides, because the hypotenuse-side works like a perfect mirror. The prism is mounted on a rotating platform, equipped with a goniometer, with the cathetus-sides and the hypotenuse-side parallel to the rotation axis. A laser beam, orthogonal to the rotation axis, impinges on the hypotenuse-side with incident angle θ_{air}. The beam transmitted into the PWO is generally split into ordinary and extraordinary beams; of the two, the ordinary beam is the more refracted. For these measurements, the incident beam was linearly polarised to completely extinguish the extraordinary component. The ordinary transmitted beam crosses the PWO and impinges on the PWO//glue//APD interface with incident angle θ

$$\theta = 45^{\circ} - arc\sin\left(\frac{\sin\theta_{air}}{n_{PWO}}\right) \tag{5a}$$

where n_{PWO} is the PWO ordinary refractive index, measurable with great precision by means of the angle of minimum deviation [14]. Starting from normal incidence orientation ($\theta_{air} = 0$), the prism is turned clock-wise (from the top view of Figure 8) until the total reflection condition is reached, at $\theta_{air} = \theta_o$ when

$$\theta = \theta_c = \arcsin(n_{glue}/n_{PWO}) \tag{5b}$$

The glue refractive index is related to θ_0 by

$$n_{glue} = n_{PWO}\sin\left(45^{\circ} - \arcsin\left(\frac{\sin\theta_0}{n_{PWO}}\right)\right) \tag{5c}$$

The refractive index of the perfectly cured *Histomount* was determined by smearing a thin layer of glue on the prism and measuring the critical angle several days later: at the wavelength of the green HeNe laser (λ = 543.5 nm) $n_{glue} = 1.590 \pm 0.002$. It may be noted that Zymed Laboratories inc. sells a similar product with the same name, but its refractive index, is lower, 1.507 ± 0.002.

The prism method was also used to monitor the glue curing. Figure 9 shows the results of the scanning of the PWO//glue//APD interface for two different gluing methods. In the first case, the PWO and the APD are compressed soon after the deposition of a drop of glue on the APD surface. The fresh glue remains enclosed between the PWO and the *Epoxy* window, as in a bottle. In the present case the *Epoxy* window was 0.18 mm depressed with respect to the border of the APD package. PWO and *Epoxy* do not absorb xylene, which can evaporate only by migrating through the glue separating the PWO and the border of the APD package. In this case even after 55 days the glue is only partially cured.

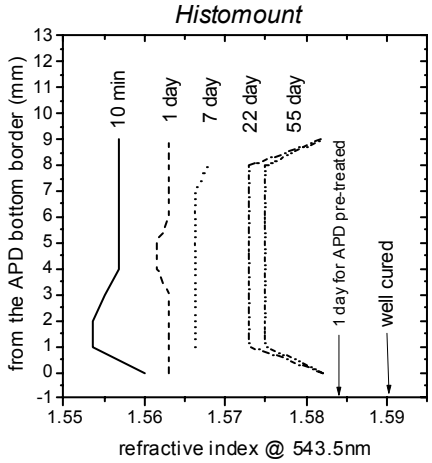


Figure 9: monitoring of the *Histomount* curing in the real condition, PWO//glue//APD

According to the second method, the surface of the APD is pre-treated by spreading a glue drop on the APD surface, and leaving it to cure for one day. Then the final gluing of the APD onto the PWO follows. Figure 9 shows that just one day after the final gluing, the refractive index is close to the well cured value and is constant along the PWO//glue interface; this indicates that the glue layer is almost completely cured. Probably if the surface of the APD window was not depressed respect to the package, the same fast curing should be observed without the pre-treatment.

The monitoring of the curing for PWO//glue//capsule, where each APD of the capsule was pre-treated, gave similar results. That indicates that the most of the xylene has evaporated after one day.

The prism method also allows the measurement of another very important characteristic: the cut-off angle of the detectable photons. As already mentioned, the cut-off angle depends on the layer with the lowest refractive index among those crossed by the photons before reaching the silicon surface of the APD. In the present version of the Hamamatsu APDs, this is the *Epoxy* window. The cut-off angle was determined by recording the APD readout versus the incident angle θ: the signal cut-off is at 42.4° ± 0.1°. Then, by equation (5b), the *Epoxy* refractive index is 1.540 ± 0.003, in good agreement with the spectrophotometric evaluation, 1.55 ± 0.01.

6 Conclusions

Among the investigated commercial optical glues, from a technical point of view *Histomount* seems to be the most suitable for CMS, fulfilling all the requirements. Gluing of prototype APDs with concave surfaces on a large scale revealed some difficulties associated with the curing of the significant volume of glue in the enclosed space (and not restricted to *Histomount*). However, the final APDs are delivered with a convex surface which is expected to eliminate these difficulties.

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