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Romain Grangeat, Marion Girard, Cyril Lupi, Dominique Leduc, Frédéric Jacquemin. Revealing of interphases in bonded joints with a fiber optic sensor based on Fresnel reflection. *International Journal of Adhesion and Adhesives*, 2019, 91, pp.12 - 18. <10.1016/j.ijadhadh.2019.02.009>. <hal-03484790>

HAL Id: hal-03484790

<https://hal.science/hal-03484790v1>

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Revealing of interphases in bonded joints with a fiber optic sensor based on Fresnel reflection

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Abstract

The interfacial zone between the polymer and the substrate is a particular area where physical or chemical bonds are established. It is important to understand the phenomenon occurring in this area, the literature highlights a possible under-crosslinking. Therefore, there is a polymerization gradient in the thickness of the adhesive joint that is called interphase. The aim of this study is to reveal this interphase by following the evolution of the polymerization rate. In general, this degree of crosslinking is determined by a differential scanning calorimetry (DSC) analysis. This study describes the steps of the kinetics of polymerization by measuring the refractive index of the adhesive. For that purpose, a fiber optic sensor based on Fresnel reflection is used. This sensor measures the evolution of the refractive index of the adhesive during the manufacturing process. To our knowledge, this is the only technique which allows *in situ* monitoring of the polymerization rate in a non-destructive manner. It is then possible to conclude on the presence, or absence of a polymerization gradient in the thickness of the bonded joint.

Keywords

Epoxides; Interfaces; Interphases; Polymerization; Optical fiber; Monitoring

1. Introduction

There are several types of structural joints, the best known are welding, riveting/bolting and adhesive bonding. This last method offers the possibility to join different materials, and enables, without alteration of substrates (drilling, heating ...), a better distribution of the stresses which makes it possible to reduce the size (thus the weight) of the structural parts. Bonding between two parts is made possible with the addition of structural adhesives mostly obtained from thermosetting reactive formulations. One challenge with this polymerization reaction is to obtain an adhesive joint in a state as stable as possible. This chemical reaction causes a change of

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adhesive's molecular structure (increase in the molar mass of molecules) and plays an important role in the mechanical properties of the assembly and service life. It is therefore essential to control this reaction. Generally the study of the crosslinking cycle is performed with a differential scanning calorimetric (DSC) analysis [1] on bulk adhesive which can be long and tedious. Zanni-Deffarges [2] showed a difference in behavior during water diffusion between bulk and bonded assembly. This difference may be due to under crosslinking of the bonded joint. It is therefore necessary to follow the polymerization of the adhesive *in situ*, in a bonded joint.

Bikerman [3] is the first to hypothesize the presence of an interphase between two materials. This zone between the polymer and the substrate is a particular zone where physical or chemical polymer/substrate bonds are established [Fig. 1]. The creation of these interphases has been the subject of a large number of studies. The reactions that occur are complex and are still actual scientific hurdles.

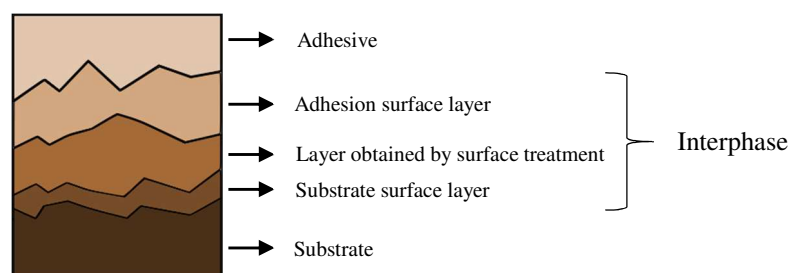


Fig. 1. Representative diagram of the interfacial zone between an adhesive and a metallic substrate

In the context of assembling metallic parts with two-component epoxy joint (epoxide/amine), many authors have highlighted adsorption reactions that can occur at the interfaces.

Hong [4] studied the interfacial region formed between an epoxide/amine adhesive and different metal substrates. They conclude that the area has been enriched with amines. Likewise other authors have observed a migration of these components towards the interfacial zone which leads to segregation of amine groups [6,7].

Roche [7] showed an increase in pH when the concentration of the amine area increases. The basic character of an epoxide/amine adhesive in liquid form ($10 < \text{pH} < 13$) may cause the dissolution of metal oxides.

Kanzow [8] and Possart [9] have shown that metal oxides can react with amines to create organometallic complexes.

All these reactions occur during the crosslinking between the epoxide cycles and the remaining amine groups. Close to the interface they cause a non-stoichiometric ratio (excess of amines). In these studies Zvetkov [10] showed a dependence between the glass transition temperature and the stoichiometric ratio of an epoxide/amine

system. In general, this temperature is lower when the ratio is not respected. It creates an interphase close to the interface that has mechanical and physicochemical properties different from bulk adhesive. For example, Aufray [11] shows a lower Young's modulus within this interphase.

The objective of this study is to highlight this under-crosslinking close to substrates. To this end, we have set up an instrumentation allowing *in situ* monitoring of the polymerization in the function of the position in the bonded joint (epoxy adhesive/stainless steel substrate): in the core of the adhesive joint and in the interfacial zone. The main idea is to follow the refractive index of the adhesive. It is highly dependent on the molecular structure of the environment. The refractive index will be measured using an optical fiber sensor based on Fresnel reflection: the Fresnel sensor. Aduriz [12] and Cusano [13] have shown a relationship between the refractive index and the rate of polymerization of an epoxy resin.

2. Materials and processing

2.1. Materials

The adhesive used in this study is commercial two-component epoxy adhesive. It consists of an epoxy resin, a hardener based on modified amines and fillers particles. During processing, a chemical reaction occurs between the epoxy resin and the hardener. In practice, the adhesive studied polymerizes under ambient conditions. To accelerate this phenomenon and obtain a complete reaction the manufacturing process is as follows: 24 h under ambient conditions followed by 24 h at 60 °C. The substrates used in this study are stainless steel (316L), the surface treatment before bonding corresponds to an industrial process: degreasing with methyl ethyl ketone followed by sandblasting.

2.2. Polymerization rate estimation – differential scanning calorimetric analysis

To control the polymerization reaction, a conventional DSC analysis was performed to determine the crosslinking rate. The polymerization rate measurements performed on the bulk adhesive are used to calibrate the refractive index measurements performed with the Fresnel sensor. To this end, samples are taken at different time during the manufacturing. A temperature rise was then made on each sample from 25 °C to 200 °C at a rate of 10 °C/min while measuring the evolution of the enthalpy of the crosslinking reaction. For each condition 3 samples were tested.

2.3. Glass transition temperature estimation – dynamic mechanical analysis

One of the specific characteristics of the polymer is the glass transition temperature: T_g . It represents the transition temperature between the glassy and rubber states. It is therefore a very important property that must be taken into account when using a polymer. This temperature is highly dependent on the crosslinking rate of the polymer. In general, a model of *Di-Benedetto* [14] is used to link these two quantities:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\alpha\lambda}{1 - (1 - \lambda)\alpha} \quad (1)$$

With α [-] the crosslinking rate

T_g [°C] the glass transition temperature

T_{g0} [°C] the glass transition temperature when $\alpha = 0$

$T_{g\infty}$ [°C] the glass transition temperature when $\alpha = 1$

λ [-] a constant parameter depending on the material where $0 < \lambda < 1$

To determine the T_g of the adhesive, dynamic mechanical analysis (DMA) tests were carried out. A temperature ramp was performed from 25 °C to 150 °C at 3 °C/min. Two load modes were used depending on the rigidity of the adhesive during polymerization processing, traction and simple cantilever.

- Tensile tests were carried out after 24 hours of crosslinking under ambient conditions and during post-cure at 60 °C. The imposed displacement at 5 µm for a useful length of 20 mm. The parallelepiped samples tested, with section 4 x 2 mm², were processed by molding.
- Cantilever tests were carried out during the 24 hours of crosslinking under ambient conditions. The distance between the two supports is 10 mm and the displacement is imposed at 10 µm. The adhesive was placed between two stainless steel substrates of 100 µm thickness.

The T_g was determined by taking the peak of the $\tan \delta$ (ratio between the loss modulus E'' and the storage modulus E') for a stress frequency of 10 Hz. In order to compare the two measurement methods, tests were repeated at 24 h and 48 h. The two load modes give similar results, with a deviation less than 1 °C.

2.4. Optical fiber sensor: Fresnel sensor

Optical fiber is a glass or plastic wire that has the ability to conduct light. It generally consists of two concentric cylinders made of silica: the core and the cladding [Fig. 2].

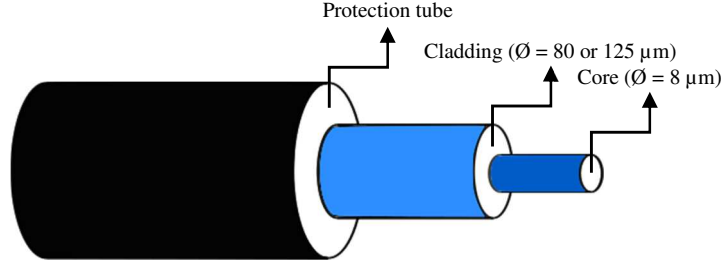


Fig. 2. Diagram of an optical fiber

The light spreads within the core. The optical fiber used in this study are single mode optical fiber (SMF28) with a core diameter of 8 μm and a cladding of 125 μm and 80 μm (Produce from iXblue IXF-SM-1550-125 and IXF-SM-1550-80). The optical characteristics used in the following (**Tab. 1**):

Cladding diameter	Refractive index $n_{\text{fiber}}(1550 \text{ nm})$	δ (Thermo-optic coefficient)
125 μm	1.457	$9.20 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
80 μm	1.451	$9.20 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$

Tab. 1. Optical characteristics (SFM28)

The thermo-optic coefficient δ represents the evolution of the refractive index in relation to the temperature. The Fresnel sensor is used to measure the refractive index of a material. In optics, the refractive index is a dimensionless number that describes how light propagates through that environment. Refractive index must be written as a complex number ($n = n + ik$), where the number k is giving the absorption properties of materials. The coefficient of reflection in intensity can then be written as:

$$R = \frac{(n_{\text{fiber}} - n_{\text{adhesive}})^2 + k^2}{(n_{\text{fiber}} + n_{\text{adhesive}})^2 + k^2} \quad (2)$$

In SiO_2 , at 1550 nm wavelength, the value of k is under 10^{-8} and the material can be considered as a transparent media, then n is considered as a real number. Secondary amines have N-H stretching that can produce absorption around 6500 cm^{-1} (1550 nm) [15]. According to the literature [16], the value of k is around or less than 10^{-3} . This means that k^2 is around 10^{-6} which is very negligible compared to $(n_{\text{fiber}} - n_{\text{adhesive}})^2$ which is at least around 10^{-2} . We can then neglect the absorption and use the classical equations [12]. In this framework, the polymerization reaction causes a change of structure (increase in the molecular weight), and therefore of the real part of the refractive index.

The polymerization reaction causes a change of structure (increase in the molecular weight), and therefore of the real part of the refractive index. By cleaving an optical fiber, and based on Fresnel reflection, it is possible to quantify the refractive index of a surrounding environment (in this study n_{adhesive}). The cleavage at the end of an

optical fiber allows the creation of a dioptric. According to *Snell-Descartes* [17] laws, a part of incident light of power P_i on the end of the fiber is reflected and provide a back reflection in the core of the fiber of power P_2 [Fig. 3].

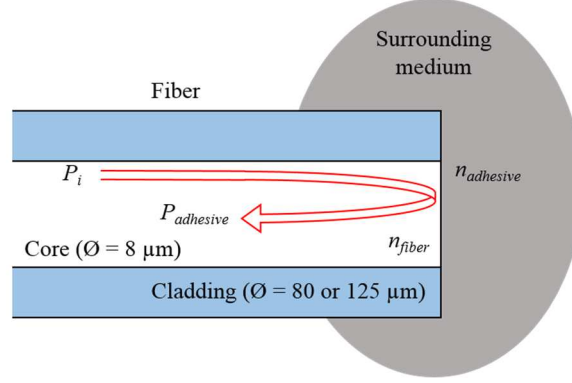


Fig. 3. Principle of the Fresnel sensor

In the literature, Cusano [13] propose to determine the refractive index by measuring the reflected power by the sensor. A first one is done in a known environment (air for example) and the second one in the targeted environment (adhesive in our case of study). The two values of reflected power are then used in equations (3) and (4) to retrieve refractive index of the unknown environment:

$$\eta = \left(\frac{n_{fiber} - n_{air}}{n_{fiber} + n_{air}} \right) \left(\frac{P_{adhesive}}{P_{air}} \right)^{\frac{1}{2}} \quad (3)$$

$$n_{adhesive} = -n_{fiber} \left(\frac{\eta + 1}{\eta - 1} \right) \quad (4)$$

With P_{air} is the reflected power when the sensor is in the air

$P_{adhesive}$ is the reflected power when the sensor is in the adhesive

In this study, the air refractive index is considered equal to $n_{air} = 1.000$. To take the measurement, a laser with 1550 nm wavelength is used. It is connected to a 2 by 1 optical coupler and the optical wave propagated through the coupler and then inside the optical fiber. The optical wave reflected by the sensor is then backscattered in the fiber and measured on a photo-receiver through the coupler. To interrogate this sensor, the setup includes [Fig. 4]:

- A laser of low coherence (1550 nm)
- An optical coupler
- A detector (photodiode + voltage acquisition system)

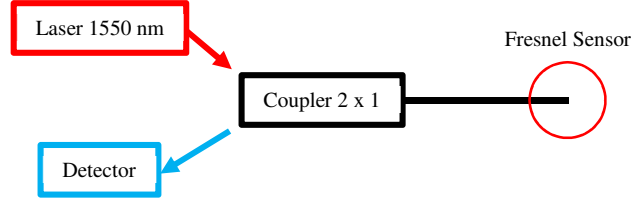


Fig. 4. Principle of measurement of Fresnel sensor

3. Results and discussion

3.1. Measurement of the physical properties of the bulk adhesive during crosslinking by conventional techniques

3.1.1. Evolution of the polymerization rate during the manufacturing process

First, DSC analysis were performed to determine the evolution of the crosslinking rate during the manufacturing process. For each time three tests were carried out. The [Fig. 5] shows a decrease in the exothermic peak during the manufacturing process.

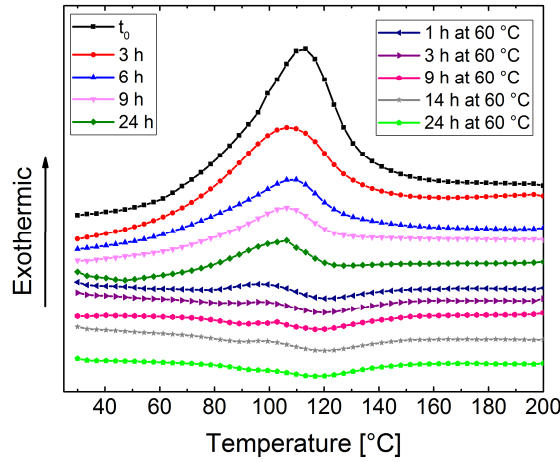


Fig. 5. Evolution of the enthalpy during the manufacturing process (from 25 °C to 200 °C at 10 °C/min)

By integrating the surface under the curves (equation (6)) of the [Fig. 5], it is possible to estimate the enthalpy of the crosslinking reaction for different processing times. Then the crosslinking rate of the reaction is calculated with equations (5) and (6):

$$\alpha(t) = 1 - \frac{\Delta H_t}{\Delta H_{tot}} \quad (5)$$

$$\Delta H_t = \int_0^t \frac{\partial H}{\partial t} dt \quad (6)$$

With $\alpha(t)$ [-] the crosslinking rate at time t

ΔH_t [J.g⁻¹] the enthalpy of the reaction estimated at time t

ΔH_{tot} [J.g⁻¹] the total enthalpy of the reaction:

$$\Delta H_{tot} = 141.25 \pm 7.13 \text{ J.g}^{-1}$$

For epoxide/amine systems, the total enthalpy of the reaction is usually measured between 175 and 500 J.g⁻¹ [1,16].

In this study, the measured value is lower. It can be explained by the presence of fillers particles within the adhesive that do not participate in the polymerization reaction.

The graph [Fig. 6] shows a first phase of polymerization during the first 24 hours under ambient conditions; the crosslinking rate reached at the end of this period is 85 %. At the end of the process, after the post-cure of 24 h at 60 °C, the reaction is completed, and the material obtained is fully polymerized.

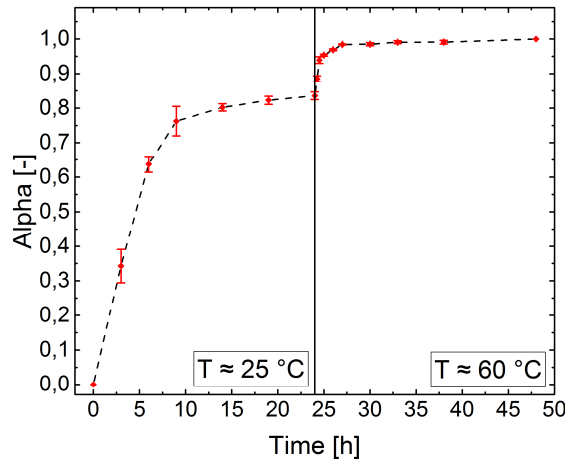


Fig. 6. Evolution of polymerization rate as a function of processing time

3.1.2. Identification of crosslinking rate versus glass transition temperature relationship

The T_g was determined by DMA using the method mentioned above. Three tests were carried out at the same time when the polymerization rate was determined [Fig. 6].

The evolution of T_g as a function of the crosslinking rate, follows a law of *Di-Benedetto* (equation (1)) [Fig. 7]:

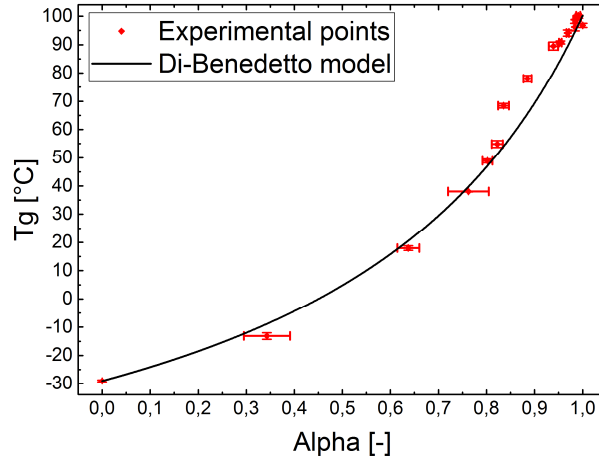


Fig. 7. Link between glass transition temperature and adhesive crosslinking rate

The parameters identified for the *Di-Benedetto* model [Fig. 7] are in the following (Tab. 2):

T_{g0} [°C]	-29.0
T_{gx} [°C]	100.2
λ [-]	0.354

Tab. 2. Identified parameters of *Di-Benedetto* model

3.2. Calibration of the Fresnel sensor on bulk material

Characteristics of the bulk adhesive, polymerization rate and glass transition are known during crosslinking. In the following section, the objective is to set up an optical fiber instrumentation in order to monitor afterwards *in situ* polymerization reaction. This requires identifying the relationship between the refractive index and the crosslinking rate.

3.2.1. Evolution of the refractive index during the manufacturing process

The experimental setup [Fig. 4] was used to measure the evolution of the reflected optical power during the polymerization of the adhesive. Using the equations (3) and (4), it is possible to calculate the refractive index of the adhesive.

The graph [Fig. 8] represents the evolution of the refractive index during the manufacturing of the adhesive. Three tests were carried out. During the first 24 hours in ambient conditions, the refractive index evolves, then, the post-cure at 60 °C causes a sudden increase. The refractive index stabilizes after 24 hours at 60 °C at 2.896.

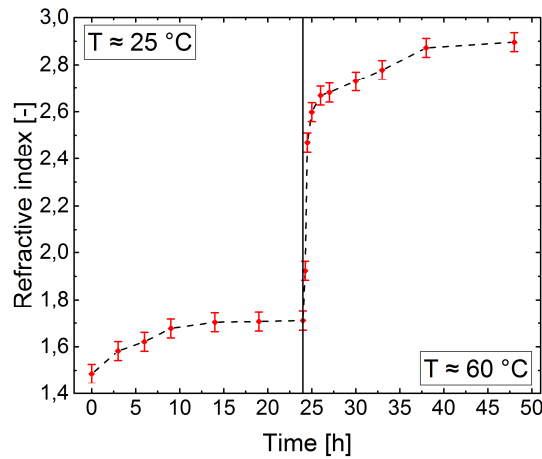


Fig. 8. Evolution of the refractive index (at 1550 nm) as a function of the processing time

At the end of the polymerization reaction, the refractive index obtained is high compared to those measured in the literature on epoxy resins (between 1.55 and 1.65) [12,17]. It is necessary to note the presence of titanium dioxide and carbon black in the commercial adhesive studied. The refractive index of these compounds have been measured in the literature and listed in the following (**Tab. 3**). We noticed also that interphase can occurred between the SiO₂ of our sensor and the adhesive [22] and can affect the value of refractive index of adhesive without glass fiber sensor. The post-cure leads to decrease the effect of absorption due to N-H stretching and makes visible the fillers particles contribution. According to the existence of the interphase and to different size of fillers and N-H, the presence of these fillers particles may explain the high value of the refractive index of the adhesive measured at the end of polymerization.

Materials	Refractive index at 1550 nm	Bibliographic sources
Titanium dioxide	2.710	[20]
Carbon black	2.393	[21]

Tab. 3. Optical characteristics of the fillers particles present in the commercial adhesive

3.2.2. Temperature correction

The refractive index of a material depends on the temperature. Aduriz (2007) [12] showed a linear evolution between the refractive index and the temperature for an epoxy resin. This evolution makes it possible to determine the thermo-optical coefficient δ . He also showed that this coefficient depends on the polymerization rate of polymer.

In this study during the process, a post-cure at 60 °C is carried out. It is therefore important to know the dependence of the refractive index on the temperature in this area ($0.83 \leq \alpha \leq 1$). For this, the evolution of the refractive index for the two extreme polymerization rates at 60 °C is determined [Fig. 9].

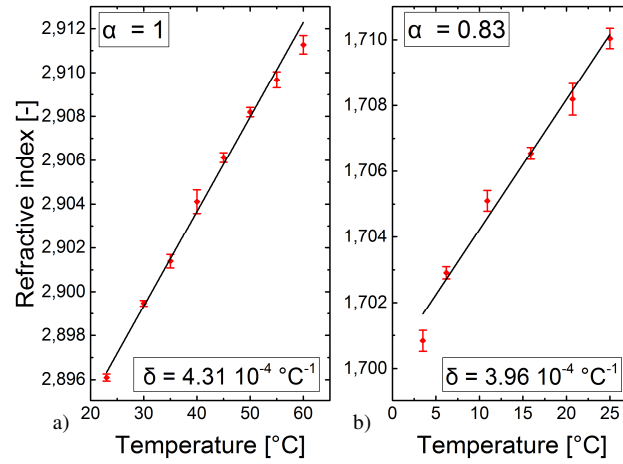


Fig. 9. Evolution of the refractive index as a function of temperature for different polymerization rates: a) $\alpha = 1$ and b) $\alpha = 0.83$

The results obtained and shown in the (Tab. 4) show that there is a dependence between δ and the polymerization rate. When the rate of polymerization increases, this coefficient also increases.

α [-]	δ [°C ⁻¹]
0.83	$3.96 \cdot 10^{-4}$
1	$4.31 \cdot 10^{-4}$

Tab. 4. Thermo-optic coefficient for different polymerization rate

In order to correct the refractive index measured during post-cure [Fig. 8], it will be considered as a linear evolution of the δ as a function of the polymerization rate. [Fig. 10] shows the corrected refractive index with temperature (a red curve).

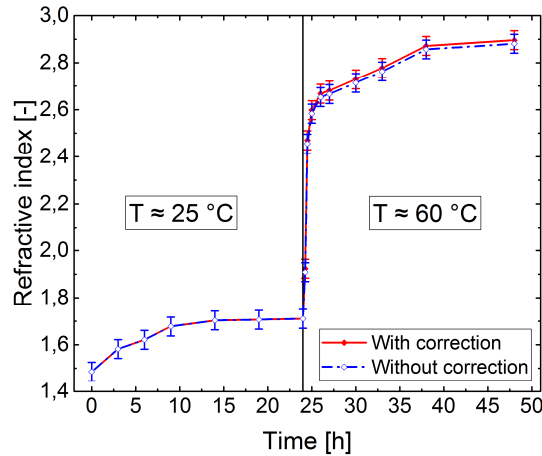


Fig. 10. Evolution of the refractive index as a function of the processing time with and without temperature correction

Afterward the measured refractive index of the adhesive will be corrected for a temperature of 25 °C.

3.2.3. Identification of crosslinking rate versus refractive index relationship

The graph [Fig. 11] shows the evolution of the refractive index as a function of the rate of polymerization of the adhesive. Using an analogy with the law of *Di-Benedetto* (7), it is possible to propose a model and identify a law [Fig. 11] to connect the two quantities:

$$\frac{n - n_0}{n_\infty - n_0} = \frac{\alpha\omega}{1 - (1 - \omega)\alpha} \quad (7)$$

With α the crosslinking rate

n the refractive index of the bonded joint

n_0 the refractive index when $\alpha = 0$

n_∞ the refractive index when $\alpha = 1$

ω a constant parameter depending on the material where $0 < \omega < 1$

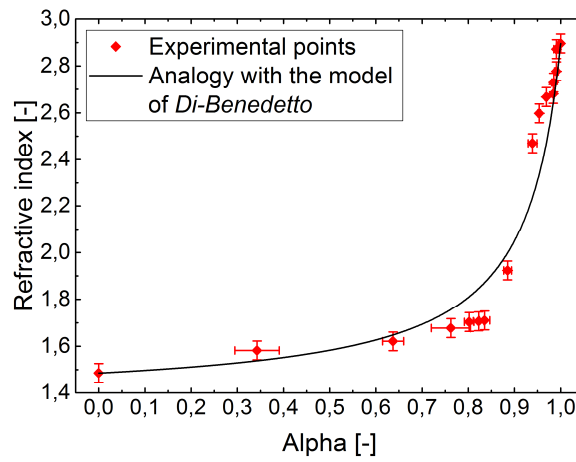


Fig. 11. Evolution of the refractive index as a function of the crosslinking rate

The parameters identified for the analogy with the *Di-Benedetto* model [Fig. 11] are in the following (Tab. 5):

n_0 [-]	1.486
n_∞ [-]	2.896
ω [-]	0.074

Tab. 5. Identified parameters for the analogy with the *Di-Benedetto* model

3.3. In situ measurement of polymerization within a bonded joint

3.3.1. Evolution of the refractive index during the manufacturing process

The approach is to position several Fresnel sensors in the thickness of bonded joint. They will be positioned at different distances from the substrate [Fig. 12]. The objective is to measure the refractive index of the adhesive in order to determine the polymerization state of the bonded joint.

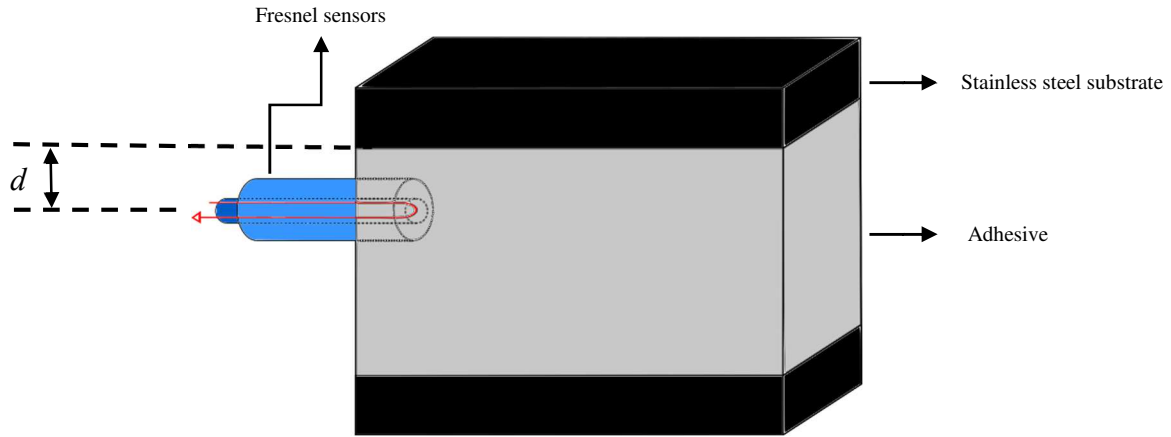


Fig. 12. Instrumentation of bonded joint with Fresnel sensors

For that, four sensors are positioned at different places (Tab. 6), and for each position three tests were carried out. These positions were verified by microscopic analysis [Fig. 13].

Sensors	Theoretical distance to substrate d	Real average positions	Cladding diameter	Fiber type
1	2000 μm	$1983 \pm 83 \mu\text{m}$	125 μm	IXF-SM-1550-125
2	125 μm	$144 \pm 11 \mu\text{m}$	125 μm	IXF-SM-1550-125
3	62.5 μm	$73 \pm 6 \mu\text{m}$	125 μm	IXF-SM-1550-125
4	40 μm	$47 \pm 4 \mu\text{m}$	80 μm	IXF-SM-1550-80

Tab. 6. Position of the sensors in the bonded joint

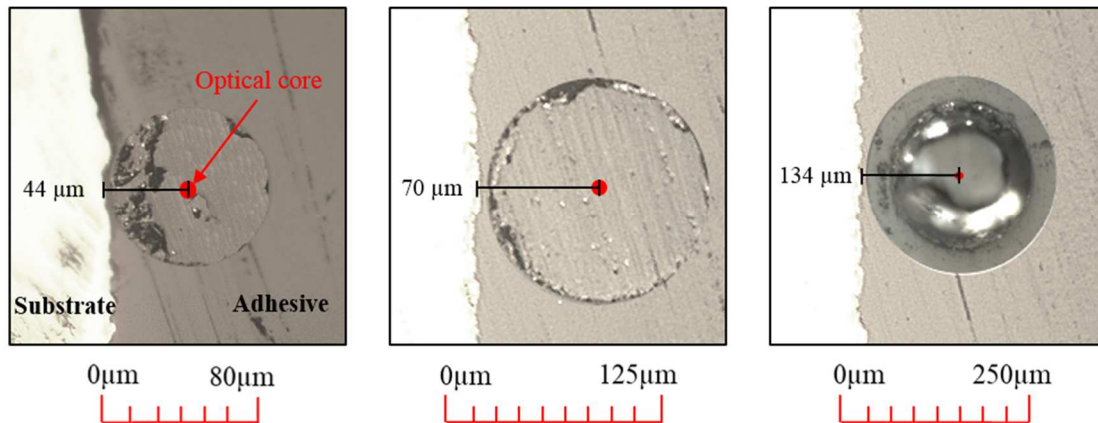


Fig. 13. Analysis by microscopic analysis, determination of the position sensors (for the following theoretical distances 40 μm , 62.5 μm and 125 μm)

Images in [Fig. 13] show the distance between the optical core (refractive index measurement area) and the stainless steel substrate.

By following the evolution of the refractive index for these four sensors the following curves were obtained [Fig. 14]:

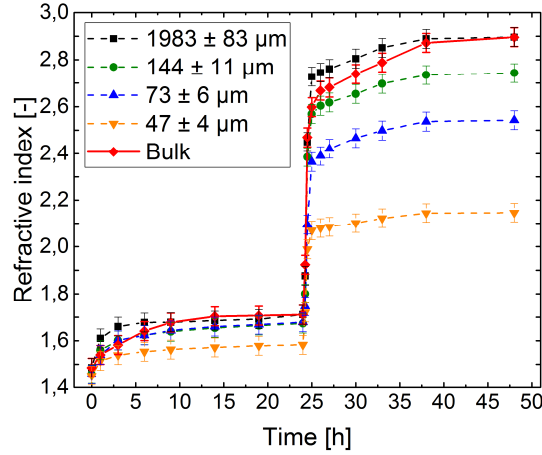


Fig. 14. Evolution of the refractive index as a function of the processing time for different Fresnel sensors in a bonded joint

The graph [Fig. 14] shows a significant difference in refractive index as a function of the distance of the sensor from the substrate. This difference in refractive index [Fig. 14] shows the presence of an interphase between the metal substrate and the adhesive. When the sensor is positioned at a certain distance from the substrate it is noticed that the measured refractive index corresponds to that determined on bulk. Concerning the nature of this zone we will make the hypothesis of under-crosslinking (lack of stoichiometric ratio).

3.3.2. Under crosslinking in a bonded joint

Assuming under crosslinking in the interfacial zone, and using the results obtained in graph [Fig. 14] and the identification [Fig. 11]. It is possible to trace the evolution of the polymerization rate at different distances from the substrate [Fig. 15].

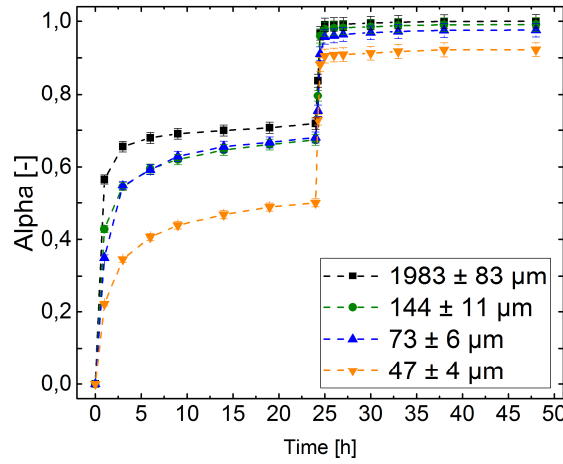


Fig. 15. Evolution of the polymerization rate as a function of the processing time for different Fresnel sensors in a bonded joint

By comparing polymerization rates at different distances from the substrate it is possible to measure T_g [Fig. 7].

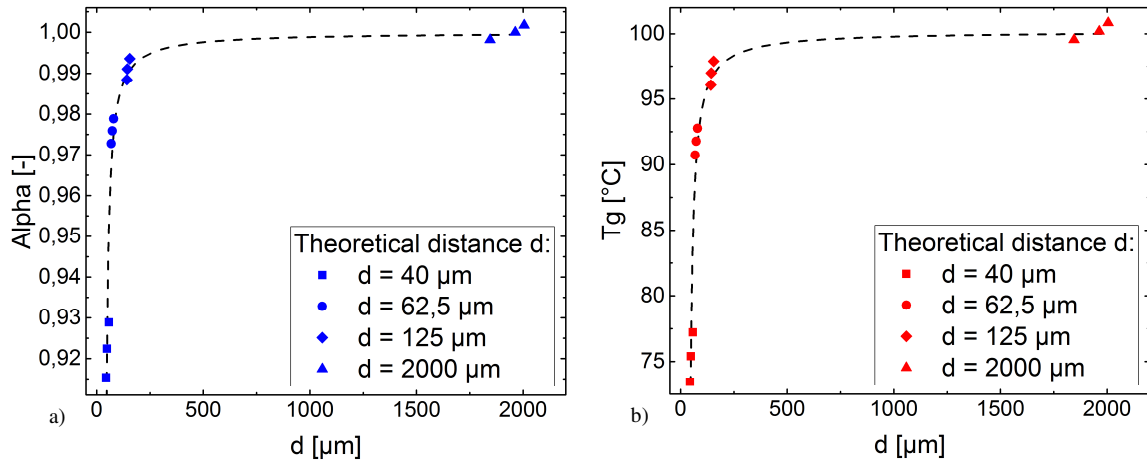


Fig. 16. Evolution of a) Alpha and b) T_g as a function of distance from the substrate

The evolution of the polymerization rate as a function of the distance to the substrate [Fig. 16-a)] shows the presence of under-crosslinking of the adhesive in the interfacial zone. This phenomenon results in the presence of a gradient of properties, including the glass transition temperature [Fig. 16-b)]. Indeed, this temperature is lower closer to the substrates than at the heart of the bonded joint.

4. Conclusion

This study highlights the possibility of controlling the polymerization reaction of an epoxy adhesive using a fiber optic sensor based on Fresnel reflection. This sensor also showed the presence of a polymerization gradient in the thickness of the adhesive joint within a bonded structure. It is possible to quantify this gradient by measuring the evolution of the glass transition temperature relative to the distance from the substrates. This result allows to

conclude on the presence of interphases. These various results demonstrate its potential and relevance for *in situ* monitoring with Fresnel sensor. This sensor made it possible to reveal the presence of interphases in a non-destructive way. Moreover, it is important to note that this optical technique is not expensive since it requires common optoelectronic components. In an industrial application, this sensor would allow monitoring of a manufacturing process by questioning the state of polymerization in the core of the bonded joint.

Acknowledgement

This study is part of the INDUSCOL project and the authors wish to associate the industrial partner of this project; Naval Group. This work benefited from France Energies Marines and State financing managed by the National Research Agency under the Investments for the Future program bearing the reference ANR-10-IED-0006-08.



ANR-10-IED-0006-08

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