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1 Article

2 Effect of thermo-mechanical ageing on materials and 3 interface properties in flexible microelectronic devices

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12 **Abstract:** The effect of thermal ageing, fatigue and thermo-mechanical ageing on flexible microelectronic
13 devices is studied and reported from a materials and functional durability perspective. The degradation
14 mechanisms of encapsulant and substrate were both studied. Property changes in encapsulant and substrate
15 materials are analyzed and their relationships in the failure mechanisms of the flexible devices determined.
16 Stiffening of the resin under thermal ageing conditions is associated with delamination in test vehicles, which
17 leads to a loss of functional electrical properties. Degradation was due to the prominence of crosslinking
18 reactions occurring during thermal oxidation at 120°C. A moderate stiffening of the resin occurs after fatigue
19 stress testing. Whereas this latter stiffening is similarly associated with crosslinking reactions, here, stiffening
20 could not be induced by thermal degradation of the resin, because the stress frequency employed was low.
21 Instead thermo-mechanical coupling occurred in two stages. Under mild conditions, the degradation
22 mechanisms correspond to the combined effect of thermal ageing and fatigue processes. Under harsher
23 thermo-mechanical conditions, the chain-scission mechanisms become more efficient and induce a softening
24 of the resin.

25 **Keywords:** Flexible microelectronics; thermo-mechanical ageing; epoxy resin; durability; encapsulation

26

27 1. Introduction

28 The development of flexible microelectronic devices has led to a blossoming of new applications. Flexible
29 microelectronics allows lightweight and conformable devices to be developed and used as biomedical implants,
30 smart textile, or sensors for the internet of things. Münzenrieder et al developed flexible and stretchable
31 oxide-based electronic sensors for skin and smart-implant uses [1]. Carta et al. designed flexible sensors for
32 monitoring biomedical parameters such as heartbeat, temperature, humidity, and respiratory rate. Most
33 commonly, such sensors were designed and embedded in smart textiles [2].

34
35 To achieve such flexibility, however, micro-electronic components have to be interconnected to
36 conformable flexible substrates. Thin, light, conformable, and flexible substrates offer a reliable alternative to
37 rigid printed circuit boards (PCB). Several studies have presented polymers such as polyethylene terephthalate
38 (PET), polyethylene naphthalate (PEN), and polyimide (PI) as suitable candidates to use as flexible substrates
39 [3–5].

40 Today, the development of flexible, stretchable, and reliable electronic circuits is an important research
41 area. Gonzalez et al. used finite element modeling to determine the geometrical stresses in the metallic
42 connection [6] and arrived at the horseshoe as the optimal geometry. In their review, Rim et al. demonstrated
43 that conductive nanoparticles, deposited via inkjet printing, can offer a suitable solution for processing flexible
44 electronics [3].

45
46 Like classical rigid electronic systems, flexible microelectronic devices are susceptible to physical
47 conditions in their working environment. Both electrical circuits and silicon chips are subject to attack by
48 humidity and oxygen from the air. To better prolong the lifetime of these devices, their microelectronic systems
49 require protection by a conformable encapsulant. Here, the encapsulant protects against physical and chemical

50 attacks from the external environment and mechanical impacts. In particular, it ensures water-tightness of the
51 system[7]. Lewis has outlined the permeability requirement for flexible electronics [8]. Although inorganic
52 encapsulants such as glass readily meet these requirements, they are particularly impractical as flexible devices.
53 Several studies have dealt with the development of flexible encapsulation systems, especially those in the field
54 of organic photovoltaics. For example, Gaume et al. developed an ultra- multilayer barrier based on polyvinyl
55 alcohol (PVA) and clay for such applications [9]. However, the durability of this multi-layer depends on the
56 long-term stability of their composite materials and interfaces. Topolniak et al. studied the ageing of ethylene
57 vinyl alcohol (EVOH)/zeolite composites for the encapsulation of flexible photovoltaics [10] and it was later
58 shown that the photo-oxidation of such composites could lead to a weakening of the barrier properties.

59 Bossuyt et al. studied the stability of flexible microelectronic devices under cyclic mechanical stretching
60 [11]. They focused on the mechanical cycling effects on the electrical properties of microelectronic devices.
61 Fatigue rupture in electrical copper traces was observable after several hundred thousand cycles.

62 Although the combined effects of thermal ageing of materials and mechanical stress can occur in many
63 flexible systems and lead to early failure, to our knowledge, only a few papers have dealt with this phenomenon.
64

65 In this paper, a flexible epoxy formulation based on ECC and EA is studied as a potential candidate for
66 encapsulation of microelectronic devices. Despite the large number of papers dealing with epoxy resin
67 durability, most have focused on bisphenol A diglycidyl ether (DGEBA) and epoxy amine-based resins [12–
68 15]. Delor-Jestin et al. [14] showed that the thermal and photochemical stability of DGEBA-based epoxy were
69 both affected by the chemical nature of the curing agent used. Ernault et al. linked the embrittlement of such
70 epoxies upon thermal ageing to changes in their glass transition temperature [13], and β -transitions [12]. The
71 β -transitions are attributable to local motions of hydroxyether groups present in DGEBA [16]. Embrittlement of
72 DGEBA-based epoxy resin is associated with changes in the transition temperature and intensity upon oxidative
73 ageing [12].

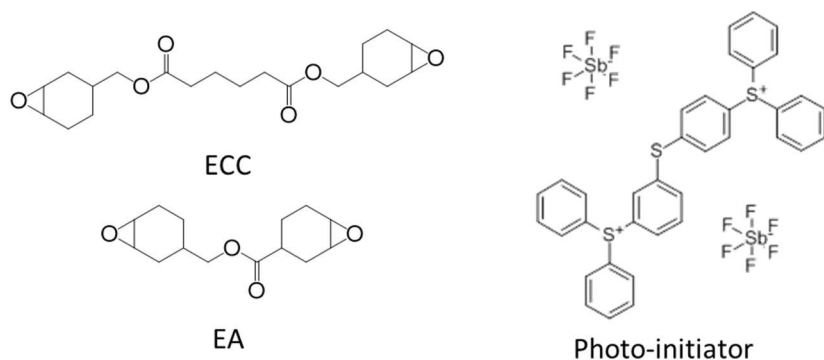
74 To be flexible and conformable requires that the chemical structure of the epoxy resins be linear and
75 saturated. Few articles have dealt with saturated epoxy ageing or used mechanical criteria to characterize
76 ageing. Dupuis et al. [17] presented the photo-oxidative degradation mechanism of linseed-based epoxy resin
77 and its effects on the surface and mechanical properties. Their results showed that for shorter irradiation times
78 (<150h), crosslinking reactions induced an increase in nano-hardness, while scission reactions become more
79 competitive at longer irradiations, resulting in a decrease in hardness. The chemical structure of the resin
80 studied mainly consisted of aliphatic chains. In our study, the chemical structure is quite different, with the
81 monomers used based on cyclohexene oxide derivatives. Thus, the main chain segment consisted of a
82 cyclohexane ring linked to an oxygen bridge. The degradation mechanisms also differ from the ones reported in
83 previous publications [14,15].
84

85 This paper aimed to identify and understand the destruction mechanisms induced in flexible smartcards by
86 environmental conditions via temperature and mechanical fatigue during their use. The effects of the
87 encapsulant and substrate ageing on the electrical performance and durability of flexible microelectronic
88 devices are presented. This work primarily focused on the polymer material behaviors as the encapsulant and
89 substrate; and the interfacial integrity between the encapsulant/substrate bilayer systems.

90 2. Materials and Methods

91 2.1. Materials

92 The epoxy resin formulation used as encapsulant (named PNE) was developed and supplied by Protavic
93 International. The formulation comprised a mixture of two monomers:
94 3,4-epoxycyclohexylmethyl-3',4'-epoxy-cyclohexene carboxylate (ECC) and 3,4-epoxycyclohexyl adipate
95 (EA). Their chemical structures are shown in Figure 1. A weight ratio of 1.5 for the ECC monomer to 1 for the
96 EA monomer was employed. Bis[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluoroantimonate) at (0.25-0.50
97 wt%), also presented in Figure 1, was used as a photo-initiator. The resin was filled with amorphous silicon
98 oxide (30-40 wt%) and cured under UV radiation.



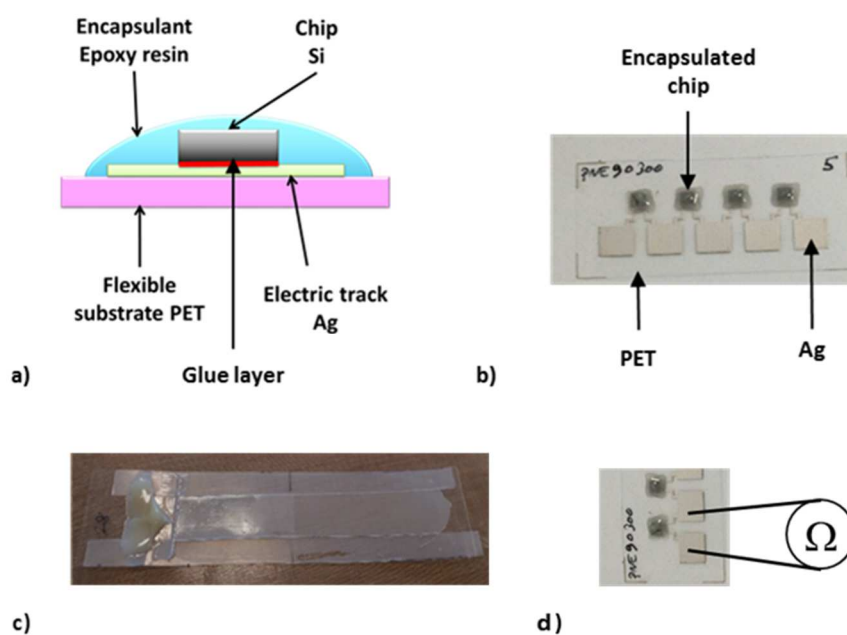
99

100 **Figure 1.** Chemical structures of the two monomers (ECC and EA) constituting the PNE encapsulant and the
 101 photo-initiator

102 *2.2. Sample preparation*

103 Commercial PET films with a thickness of 120 μm were selected for their flexibility and used as the substrate.
 104 A silver electrical circuit was deposited on the substrate and a silicon chip glued to it (Figure 2 a). These
 105 systems, called Test Vehicles (TV), were supplied by STMicroelectronics. TVs were encapsulated using a glob
 106 top of the PNE resin (Figure 2 b). The glob top architecture, chosen because it advantageously minimizes the
 107 amount of protective polymer, also reduced delamination damage by ensuring a lower interfacial surface
 108 contact with the substrate. Resin deposition was conducted in a clean room and employed an industrial Asymtek
 109 C-341 automatic dispenser. Curing used a 365 nm UV LED for 30 seconds at room temperature under an air
 110 atmosphere.

111



112

113 **Figure 2.** (a) Schematic side view of the glob top encapsulated TV showing the architectural ensemble, (b) TV
 114 encapsulated within the PNE resin, (c) multilayered PET and PNE ensemble for the peeling test, and (d) schematic
 115 top-view illustrating the experimental assembly of the resistance measurements

116 Thin 100 μm -thick free-standing epoxy resin films were deposited by bar-coating using an Erichsen Coatmaster
 117 model 510 film applicator on a Teflon® sheet. Curing was done in an Eleco model LED Cube 100 UV LED
 118 chamber, at a 365 nm wavelength for 90 seconds at room temperature under an air atmosphere.

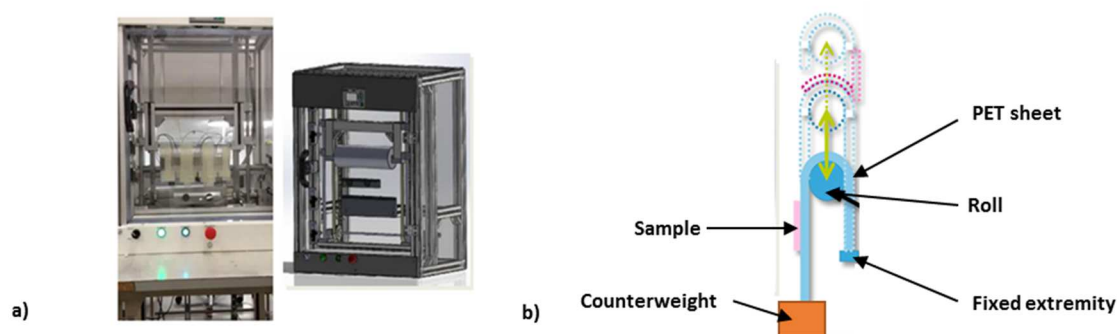
119 Multilayer samples were prepared and used to study the interfacial quality of encapsulant/substrate bilayers
 120 using the peeling test (Figure 2 c). Epoxy resin films (17 mm width, 100 μm thick) were deposited on PET
 121 substrate film (120 μm thick) and cured under the same conditions as the free-standing films.

122 DSC analysis was employed to verify that the epoxy resin was 100% cured. No residual precursor was detected.

123 2.3. Ageing conditions

124 A total of six ageing conditions were performed based on industrial requirements for smartcard applications.
 125 Thermal ageing was carried out in a ventilated oven at 120°C for up to 500 hours. Since there is no ageing
 126 temperature definition in the ISO10373 standard, the project partner STMicroelectronics proposed conducting
 127 thermal ageing at 120°C as recommended for microelectronics devices. This temperature also allowed the
 128 simulation of localized heating points that often appear in materials and interfaces during long-term mechanical
 129 fatigue tests.

130 Mechanical fatigue involved the imposition of bending cycles on the test samples by winding them around a
 131 roller at a constant frequency of 24 cycles per min, at room temperature. Ageing involved using a homemade
 132 bending bench (Figure 3 a). The principle of the mechanical tests is shown in Figure 3 b. Samples were rolled
 133 (5 000 cycles) around a 50 mm diameter roller (F1) and then subjected to optical microscopy or electrical
 134 testing. If no degradation was noticeable, the samples were again rolled (5 000 cycles) around a 25 mm
 135 diameter roller (F2).



136 a) Photograph and (b) schematic illustration of the functional principle of the bending bench
 137 **Figure 3.** (a) Photograph and (b) schematic illustration of the functional principle of the bending bench

138 Thermo-mechanical coupling analyses involved subjecting the thermally aged sample to fatigue tests. Samples
 139 initially treated for 500 hours at 120°C, were subjected to 5 000 bending cycles around a 50 mm diameter roller
 140 (TM1), followed by another 5 000 bending cycles around a 25 mm diameter roller (TM2).

141 All ageing conditions performed on the samples are reported in **Table 1**. The results presented in this paper
 142 were obtained by analyzing up to 7 samples and 4 TVs per condition.

143 **Table 1.** Ageing conditions and the number of samples used in this study

AGEING TYPE	REFERENCE	THERMAL	FATIGUE		THERMO-MECHANICAL	
CONDITION	Pristine	Up to 500h at 120°C	5000cy ø50	5000cy ø50 + 5000cy ø25	500h 120°C + 5000cy ø50	500h 120°C + 5000cy ø50 + 5000cy ø25
NOTATION	Ref	Xh*	F1	F2	TM1	TM2
Total number of sample	4 TV 7 film samples	4 TV 7 film samples	4 TV 6 film samples	4 TV 7 film samples	4 TV 7 film samples	4 TV 7 film samples

144 * X is the ageing time in hours

145 2.4. Characterization methods

146 DSC measurements were performed on a Mettler Toledo DSC 1 apparatus under an air atmosphere. Sample
 147 masses of 10 mg were placed in aluminum DSC crucibles and subjected to two heating-cooling cycles from
 148 30°C to 250°C at a rate of 10°C/min. DSC analyses allowed us to ascertain curing completion and to monitor
 149 changes in the microstructure after ageing. The crystallinity rate (χ_c) for the PET substrate was calculated using
 150 a melting enthalpy for 100% crystalline PET of 140 J/g, in line with the literature [18].

151 Dynamic mechanical thermal analyses were done on a TA Instruments DMA Q800 under air. Rectangular
 152 shaped (18 mm x 9 mm) and 100 μm thick samples were analyzed. A tensile dynamic strain of 0.1% was
 153 imposed on the samples at a frequency of 1Hz. The samples were heated from -100°C to $+100^\circ\text{C}$ at a rate of
 154 $3^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) and the β -transition were determined using the loss modulus
 155 thermograms. The full width at half maximum (FWHM) of the peaks was also determined.

156 Tensile tests were carried out on an Instron Microtester 5948 equipped with a 2 kN force cell. Three 100 μm
 157 thick rectangular samples (1.7 cm*10 cm) cut from free standing films were analyzed at room temperature,
 158 under NF ISO527-3 standard. The preload was 0.5 N and the tensile speed $5 \text{ mm}\cdot\text{min}^{-1}$. Three specimen for
 159 each ageing condition were analyzed.

160 Thermo-gravimetric analyses (TGA) were performed on a Setaram Setsys 16/18 apparatus under an air
 161 atmosphere. Sample masses of 5 mg were heated from 25°C to 700°C at a rate of $10^\circ\text{C}/\text{min}$. TGA analyses were
 162 employed to determine and monitor the degradation temperature corresponding to a mass loss of 5%.

163 Fourier transform infrared analyses (FTIR) were performed on 20 μm thick films in transmission mode with a
 164 JASCO FT/IR-6800 spectrophotometer. FTIR spectra used 32 scan summations at a 4 cm^{-1} resolution.

165 Determination of epoxy resin adhesion strengths on the PET substrate involved peeling tests performed at a
 166 peeling angle of 90° at room temperature. The peeling strengths were directly measured using an Instron
 167 Microtester 5948 mechanical testing machine equipped with a 2 kN force cell and a specifically designed
 168 peeling bench. The applied load was monitored continuously during epoxy film peeling, at a constant
 169 displacement rate of 5 mm/s. The peeling force was determined using:

$$170 \quad G = F \times (1 - \cos \theta) / w$$

171 where G is the peeling force (in N/cm), F is the applied load in the stationary domain (in N), θ is the peeling
 172 angle (here 90°), and w is the epoxy resin band width (in cm). Three samples for each ageing condition were
 173 measured.

174 Optical microscopy was performed on A Keyence VHX-1000 microscope and employed a 100X optical
 175 magnification. The magnification used enabled delamination or formation of cracks to be detected.

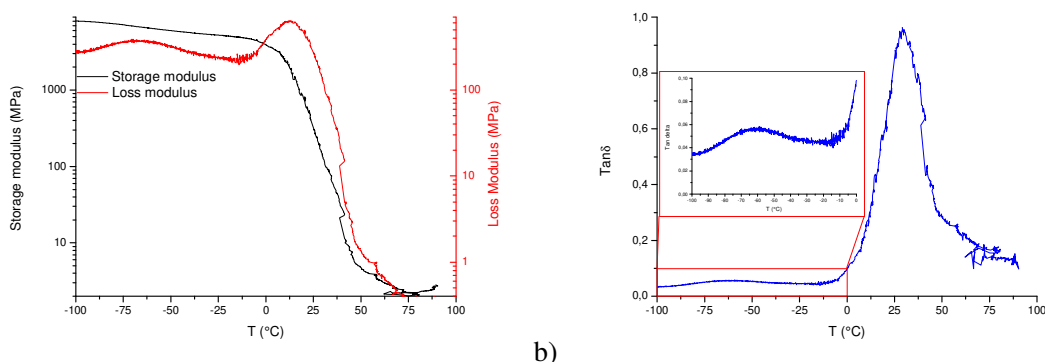
176 Confocal Raman spectroscopy allowed for the in depth chemical structural changes during ageing to be studied.
 177 The depth profiles of TV were performed starting from the substrate down to the encapsulating resin. The
 178 recorded Raman spectra with an InVia Renishaw microscope used the 633 nm laser line. To allow for analysis
 179 of the substrate and then the epoxy resin, samples were placed with the substrate on top. The spectra were
 180 recorded at room temperature with various focalizations, from 10 μm for the surface to 200 μm for deep inner
 181 sample visualizations at 10 μm intervals.

182 To detect TV functional failures, electrical tests that involved measuring the electrical resistance between the
 183 terminals of the chip (Figure 2 d) were performed. A Fluke 175 true RMS multimeter was used. An increase in
 184 the value measured corresponded to device failure and thus defined as the end of life criteria for TV in our
 185 study.

186 3. Results and discussion

187 3.1. Epoxy resin characterization

188 Ageing-induced changes of the PNE epoxy resin were determined through thermal and mechanical
 189 properties using DMTA, tensile tests and TGA.



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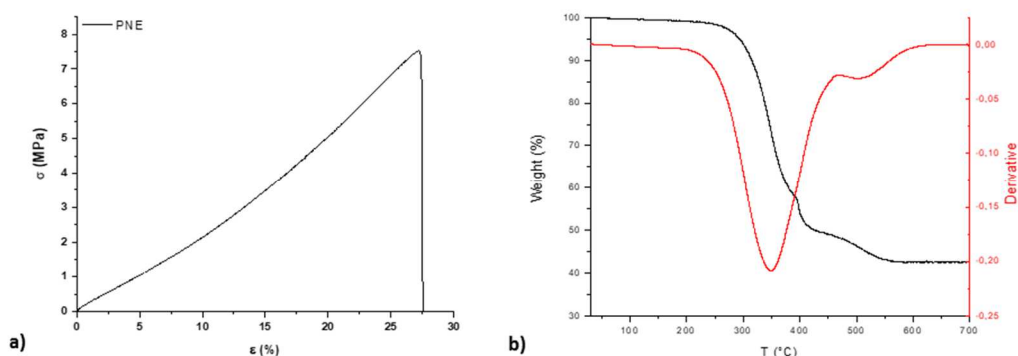
a)

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Figure 4. DMTA thermograms of unaged PNE epoxy resin showing, (a) storage and loss modulus; and (b) $\tan \delta$

192 DMTA thermograms of the epoxy resin are presented in Figure 4. The main peak of the loss modulus
 193 thermogram (Figure 4 a) is centered at +13°C. This peak is attributable to the glass transition of the PNE resin.
 194 A secondary maximum at -67°C is attributable to the β -transition of the resin. Udagawa et al. studied the
 195 dynamic mechanical properties of UV-cured ECC and EA [19] and attributed the presence of β transition in
 196 both polymers to molecular motions of the cyclohexyl rings. As the same chemical structures are present in
 197 PNE resin, its β -transition is attributable to the same molecular motions.

198 Mechanical properties were determined at room temperature using tensile test measurements. Figure 5
 199 presents a stress-strain curve for the PNE epoxy resin. Epoxy resin films exhibited a brittle break. Both Young's
 200 modulus and strain at break were determined. The resin films presented Young's modulus (E) of 33 ± 1 MPa
 201 and a strain at break (ϵ_B) of 22.9 ± 1.1 %.



202
 203 **Figure 5.** (a) Stress-strain curve and (b) TGA thermogram of unaged PNE resin film

204 The TGA thermogram of the PNE resin film is presented in **Figure 5 b**. Epoxy resin decomposition was at
 205 a temperature (T_d) of 294°C. On the derivative curve, two minima were identified at 349°C and at 503°C.
 206 Thermal degradation occurred in two stages. At the end of the experiment, 42.5 % of the original weight
 207 remained, corresponding to the silicon oxide fillers that do not degrade at these temperatures. Thus, suggesting
 208 that the filler content in the studied samples was 42.5 wt%.

209 3.2. Thermal ageing

210 Below, the effects of thermal ageing on the encapsulant and the substrate are discussed. Chemical and
 211 mechanical analyses for each specimen type are presented.

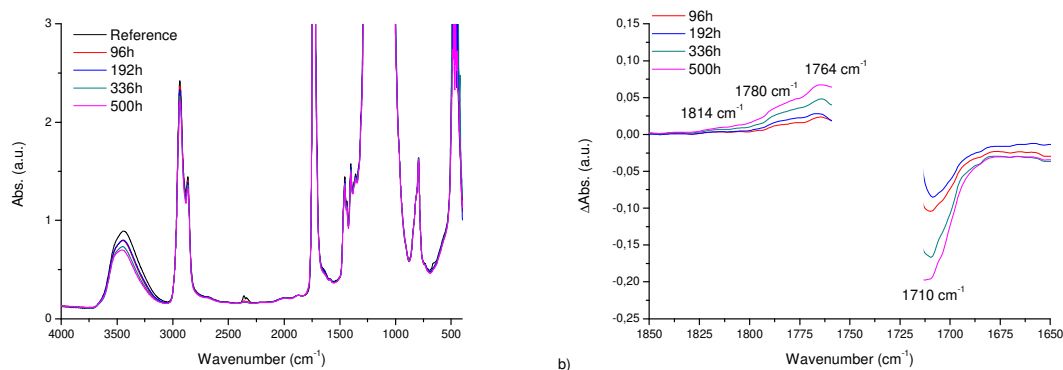
212 3.2.1. Epoxy resin ageing

213 It is important to note that the resin films presented yellowing upon ageing, indicating an alteration of their
 214 chemical structure. The evolution of the FTIR spectra with thermal ageing conditions is presented in **Figure 6**.
 215 The spectral differences (x hours - reference) in the carbonyl domain (1850 - 1650 cm^{-1}) are also presented. A
 216 white box hides a saturated part of the spectra to facilitate reading. Spectral band formation (upwards) and
 217 disappearance (downwards) were detectable on difference spectra.

218 The main change visible on the original spectra was the decrease in the broad band for wavelengths over
 219 3000 cm^{-1} . This band is attributed to O-H bonds from adsorbed water or alcohol present in the film. Amid the
 220 carbonyl domain, was observed the formation of bands at 1814 , 1780 and 1764 cm^{-1} . Whereas the vibration
 221 band at 1780 cm^{-1} corresponds to lactones formations [20], the bands at 1814 and 1764 cm^{-1} were attributed to
 222 anhydride acids formation.

223 A decrease in intensity of the band at 1710 cm^{-1} was noticeable. This band signaled the presence of
 224 ketones that degrade during thermal ageing.

225 Although these attributions relied on a reference table and previous literature findings, they should be
 226 confirmed by complementary analysis such as chemical derivatization treatments with NH_3 , SF_4 or
 227 2,4-dinitrophenylhydrazine (2,4-DNPH) [21,22]. Based on their specific reactivity with the different carbonyl
 228 functional groups, these treatments used together with FTIR analysis can identify contributions to the carbonyl
 229 band. NH_3 is reactive with esters, carboxylic acids and anhydrides; SF_4 with carboxylic acids; and the
 230 2,4-DNPH with aldehydes and ketones.



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Figure 6. Changes in the epoxy resin films with thermal ageing time (a) full FTIR spectra and (b) FTIR difference (xhours-reference) spectra for the carbonyl domain (1650-1850 cm^{-1})

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Table 2 summarizes changes in the thermo-mechanical properties of the resin upon thermal ageing. The T_g and the β -transition were determined using DMTA. The FWHM of the peaks was also calculated. Whereas the T_g increased following thermal ageing, its FWHM remained unchanged. The β -transitions were unaffected by the thermal ageing.

The Young's modulus was four times higher after thermal ageing while the strain at break decreased by a third. This change was well reflected through observed stiffening and embrittlement of the resin films.

The decomposition temperature of the resin increased from 294°C to 307°C.

241

242

Table 2. Changes in PNE resin characteristics (T_g , T_β , E , ϵ_B , T_d) induced by the different ageing conditions

Ageing	T_g	FWHM of T_g	T_β	FWHM of T_β	E (MPa)	ϵ_B (%)	T_d
Reference	13°C	23.1°C	-67°C	36°C	33 ± 1	22.9 ± 1.1	294°C
500h 120°C	26°C	24.2°C	-67°C	38°C	133 ± 32	15.1 ± 1.2	307°C
F1					50 ± 6		
F2	14°C	23.1°C	-71°C	49°C	56 ± 11	15.7 ± 2.2	295°C
TM1	28°C	31.4°C	-67°C	42°C	153 ± 21	17.8 ± 3.7	301°C
TM2	20°C	21.5°C	-69°C	50°C	126 ± 20	20.2 ± 1.0	306°C

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Polymer degradation mechanisms in the presence of oxygen involve both crosslinking and chain scissions reactions. These reactions are antagonistic and their kinetics are not identical and can vary according to the degree of degradation, ageing conditions and the nature of the polymer. Crosslinking reactions are usually linked to increases in both Young's modulus and T_g [23,24], whereas chain scission reactions have the opposite effect.

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The marked stiffening of the resin studied, coupled with the increase in its glass transition temperature during thermal ageing, could be explained by the dominance of crosslinking reactions over chain scissions in the thermal oxidation mechanism. This result is verifiable by the observed increase in the decomposition temperature, as observed by TGA. It is shown that crosslinking reactions during ageing significantly increase the polymer degradation temperature [25]. Dupuis et al. reported similar result from a study on the photo-degradation mechanism of linseed-based epoxy resin [17]. They showed that crosslinking reactions control degradation for shorter ageing times (200h) and are associated with marked increases in the modulus.

Ernault et al. linked the embrittlement of DGEBA/TTDA and DGEBA/IPDA during thermal-oxidative degradation to crosslinking reactions and β -transition intensity decrease [12]. They attributed intensity decreases in the β -transition to the oxidation of the hydroxypropylether groups of DGEBA since their local motions corresponds to this transition. In the present study, β -transitions for the PNE resin were not affected by thermal ageing at 120°C for 500h. As this transition corresponds to the cyclohexyl ring motions, the molecular mobility of this moiety should be exempt from the thermal-oxidative degradation of the epoxy resin.

261

3.2.2. PET substrate ageing

262 To better decipher the events that underpin the ageing of the bilayer assembly, PET substrate films were
 263 aged using the same conditions.

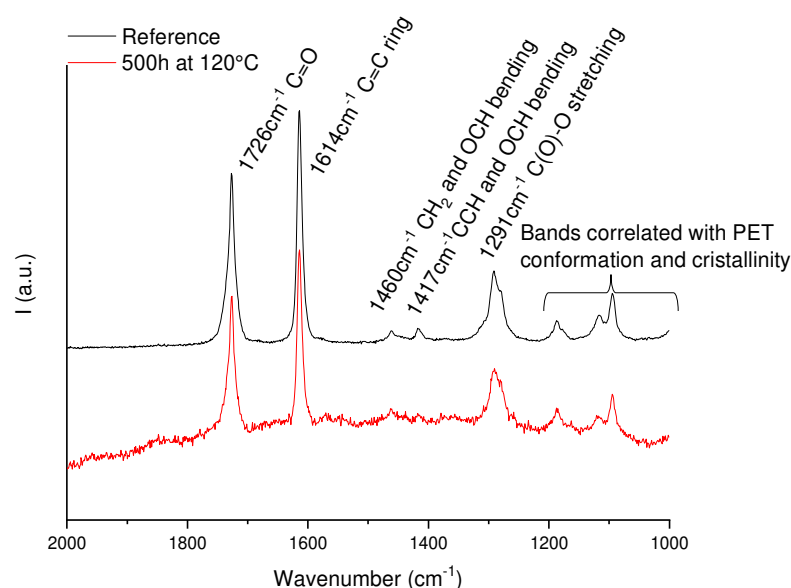
264 The mechanical and thermal properties of PET films both before and after 500h at 120°C are summarized
 265 in **Table 3**. The Young's modulus, the strain at break and the melting temperature (T_m) remained unchanged
 266 after thermal ageing. PET crystallinity increased slightly, presumably as a result of thermal annealing.

267 **Table 3.** Changes in mechanical and thermal properties of PET films induced by the different ageing
 268 conditions

Ageing	E (MPa)	ϵ_B (%)	T_m	χ_c (%)
Reference	5049 ± 42	72.7 ± 5.7	258°C	28%
500h 120°C	5116 ± 289	71.0 ± 17.6	256°C	32%
F1	5212 ± 177	71.8 ± 2.1	257°C	35%
F2	5538 ± 42	74.4 ± 8.6	257°C	30%
TM1	4932 ± 250	61.1 ± 20.2	256°C	33%
TM2	4828 ± 312	72.0 ± 11.3	256°C	34%

269 The Raman spectra of the PET substrate before and after 500h at 120°C are presented in **Figure 7**. The
 270 initial spectrum exhibits the conventional vibration bands of PET [26,27]. There was no spectral modification
 271 after thermal ageing. Instead, a broad peak covering the entire scan range appeared. However, the chemical
 272 structure of the PET substrate film should not be modified by thermal ageing under these thermal ageing
 273 conditions. Thus, the observed peak broadening is probably due to the fluorescence that emanates from the
 274 adjacent PNE layer (see description in the next part).

275 After thermal ageing at 120°C for 500h, the chemical structure and mechanical properties of the PET
 276 substrate films were conserved. The parameter change of note was an increase in PET crystallinity, possibly due
 277 to the annealing process.



278
 279 **Figure 7.** Raman spectra of PET substrate TV before (Reference) and after thermal ageing at 120°C for 500h

280 3.2.3. Bilayer and test vehicle ageing

281 PET/PNE bilayer systems and TV were all thermally aged under the same conditions. The bilayer systems
 282 were employed to characterize thermal ageing on the interface quality between encapsulant and substrate. TVs
 283 were used to determine the effects of thermal ageing on their functional properties (*i.e.* electrical properties).

284 The results of the peeling tests performed on bilayer systems are presented in **Table 4**. An adhesive
 285 rupture was observed both before and after ageing. The value of the peeling force G increased after thermal
 286 ageing at 120°C for 500h. The changes observed followed the same trend as both the T_g and mechanical
 287 properties of the epoxy resin while the substrate properties remained unchanged. The crosslinking reactions

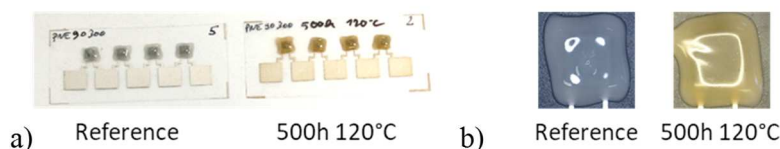
288 occurring in the epoxy resin during thermal ageing led to an increased peeling strength, although the exact
 289 mechanism that underlies this phenomenon remains unclear. Accordingly, complementary experiments are
 290 needed to decipher this mechanism and those will be the subject of a separate study.

291 **Table 4.** Changes in the peeling force between PET and PNE films induced by the different ageing
 292 conditions

Ageing	G (N/cm)	ΔG (N/cm)	Rupture
Reference	1.74	0.15	Adhesive
500h 120°C	2.70	0.14	Adhesive
F1	1.63	0.11	Adhesive
F2	1.72	0.05	Adhesive
TM1	2.61	0.19	Adhesive
TM2	2.50	0.16	Adhesive

293 Both unaged and thermally aged TV successfully passed the electrical test (**Table 5**).

294 After thermal ageing, the epoxy resin deposited on TV presented marked yellowing (**Figure 8**), whereas
 295 the PET substrate was unchanged. Similar results were obtained after free films ageing.



296

297 **Figure 8.** (a) Photographic image of a TV and (b) optical micrograph of an encapsulated chip before
 298 (Reference) and after thermal ageing (500h 120°C)

299 Confocal Raman spectroscopy was relied upon for the depth profiles needed to identify aged-induced
 300 changes in the chemical structure of the polymers used in TV. The results are presented in **Figure 9**.

301 Two areas are distinguishable on the reference TV. Intense vibration bands attributed to the PET substrate
 302 were detected for depths from 0 to approximately 100 μm . There were no identifiable vibration bands for
 303 depths over 100 μm . The Raman signal of the studied epoxy resin was very low compared to that of PET.

304 A broader vibration band for depths greater than 100 μm (*i.e.* in the epoxy resin area) for thermally aged
 305 TV was evident. This band presumably arises from fluorescent groups derived from the chemical degradation of
 306 the epoxy resin. Indeed, samples undergoing yellowing were also the ones that exhibited Raman spectra
 307 modified by fluorescence due to the thermal oxidation of the polymer. The yellowing of polymers during
 308 oxidative ageing has already been described [28–30]. Moreover, fluorescent oxidation products can form in
 309 polymer materials during oxidative ageing [31,32]. Accordingly, the fluorescence serves as an indicator of the
 310 formation of oxidation products during thermo-oxidative ageing. These results are verifiable through FTIR
 311 analytical results obtained on aged PNE films.

312

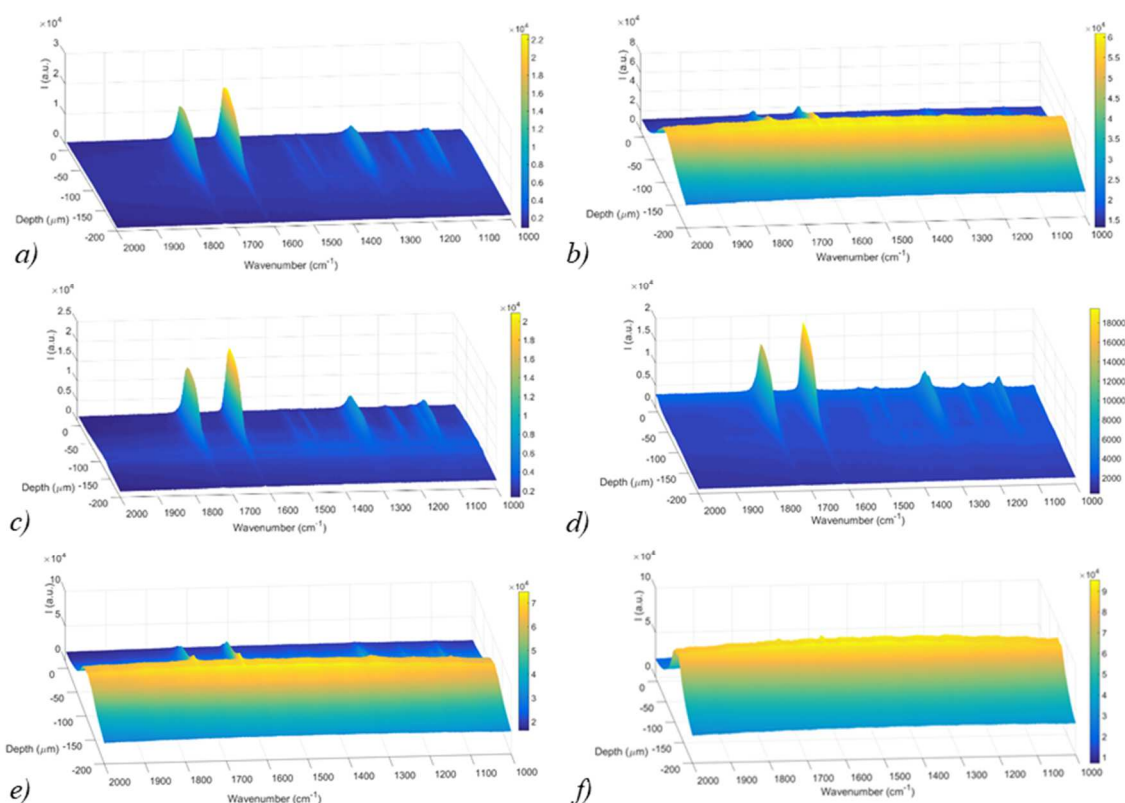


Figure 9. Raman depth profiles of TVs a) before; and after ageing under b) 500h, c) F1, d) F2, e) TM1 and f) TM2 conditions

313
314
315

316 A stiffening of the epoxy resin coupled with an increase in both T_g and T_d after thermal ageing at 120°C for
317 500h, were evidenced, as previously discussed. Such changes are associated with the dominance of crosslinking
318 reactions. Changes in the epoxy chemical structure were apparent from the yellowing of the films and the
319 formation of fluorescent oxidation products. Additionally, the PET substrate was shown to be stable, both from a
320 chemical and mechanical perspective.

321 The force needed to peel the epoxy resin from the substrate increased due to the crosslinking reactions
322 occurring during thermal ageing. TV functional properties were not affected by this reinforcement because the
323 intensity of the increase was not sufficient.

324 3.3. Mechanical fatigue

325 3.3.1. Epoxy resin fatigue

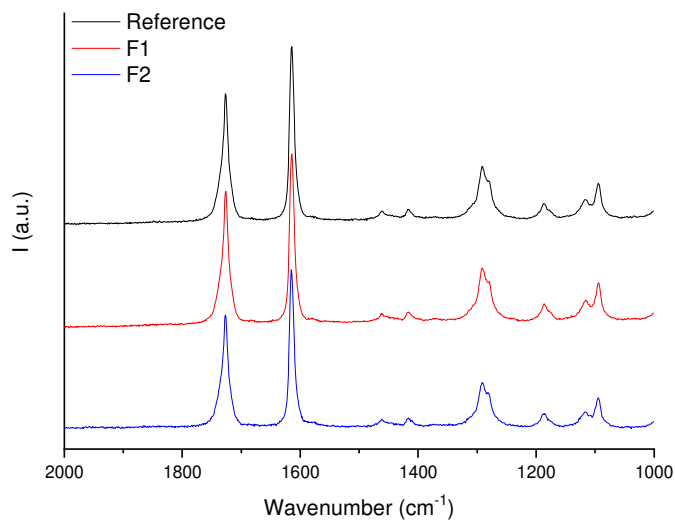
326 The thermal and mechanical properties of the epoxy resins, following fatigue ageing under F2 conditions
327 were determined using DMTA, tensile tests and TGA. The corresponding results are presented in **Table 2**.

328 The Young's modulus increased from a reference value 33 ± 1 MPa to 50 ± 6 MPa after fatigue ageing
329 under F1 conditions, indicating a stiffening of the films. However, the stiffening recorded under F1 condition
330 remained modest upon comparison, with the 133 ± 32 MPa recorded for thermal ageing at 120°C for 500h.
331 Between F1 and F2 fatigue ageing conditions, PNE films stiffening increased further. Fatigue ageing under F2
332 conditions did not affect the glass transition (T_g), β -transition (T_β) or decomposition (T_d) temperatures.
333 Additionally, the thermo-mechanical properties of PNE resin films were not significantly affected by fatigue at
334 room temperature. In order to confirm these trends, fatigue experiments should be either continued under the
335 same or harsher conditions.

336 3.3.2. PET substrate fatigue

337 The evolution of the PET substrate films properties subjected to mechanical fatigue appears in **Table 3**.
338 After fatigue ageing, the PET Young's modulus increased reflecting a stiffening of the substrate. The
339 crystallinity ratio was modified, whereas the melting temperature was unchanged.

340 Micro-Raman spectra, obtained for PET substrates before and after mechanical fatigue under F1 and F2
 341 conditions, are presented in **Figure 10**. Raman spectra after fatigue testing at ambient temperature remained
 342 unchanged, suggesting that the PET chemical structure was stable under these conditions.



343

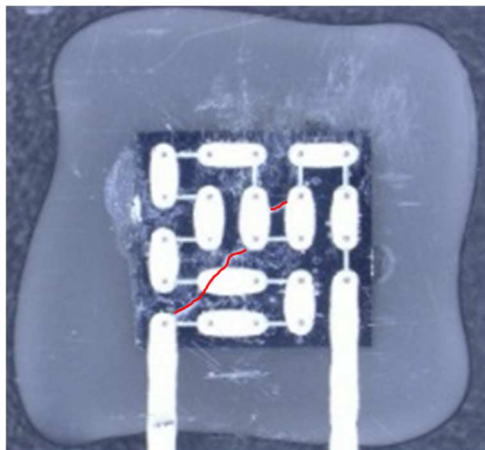
344 **Figure 10.** Changes in micro-Raman spectra of PET substrate in TVs before and after mechanical ageing under
 345 F1 and F2 conditions

346 The observed stiffening of PET after F1 is well explained by the increase in crystallinity in the polymer.
 347 However, the additional increase of stiffening, indicated by an increase in Young's modulus after F2, is
 348 nonetheless accompanied by a marked decrease in crystallinity back to its initial value. Another stiffening
 349 mechanism is involved in this case. The additional stiffening mechanism is presumably due to the presence of
 350 crosslinking reactions. For both F1 and F2 fatigue conditions, there was no sign of a modification of the
 351 chemical structure of PET. However, the chemical bond formed by the crosslinking reaction might not be active
 352 in Raman spectroscopy. Accordingly, complementary analyses are required to confirm the presence of
 353 crosslinking reactions.

354 3.3.3. Bilayer and test vehicle fatigue

355 The change in peeling force G between the PET substrate and PNE resin with fatigue ageing is reported in
 356 **Table 4**. The peeling force G remained stable after mechanical ageing, and adhesive ruptures were observed for
 357 each condition and each sample tested. The interface quality was unaffected under the fatigue conditions of the
 358 study.

359
 360 TVs electrical testing after fatigue in condition F1 was positive. However, the tests were negative after
 361 condition F2 (**Table 5**), indicating a discontinuity in the electrical circuit. Under these harsher conditions, TV
 362 failure was observed even earlier, after 5 000 cycles on the 50 mm diameter roll followed by 3 000 additional
 363 cycles on the 25 mm diameter roll. Optical microscopy was performed on TVs to determine the origin of these
 364 failures. **Figure 11** presents a microscopic image of a chip on a TV that failed the electrical test. This
 365 micrograph was captured through the transparent PET substrate to examine the electrical circuit under the chip.
 366 For this micrograph, cracks (denoted as red lines) formed within the glue layer at the substrate and the chip
 367 interface, under the harshest condition during mechanical ageing. These cracks are probably due to the marked
 368 differences in stiffness between the silicon chip and the PET film. Under these conditions, stress accumulates in
 369 the glue layer leading to cracking.



370

371 **Figure 11.** Optical micrograph of a TV after it was subjected to fatigue ageing under F2 conditions

372 The micro-Raman depth profile of TV subjected to fatigue under F1 and F2 conditions are presented in
 373 **Figure 9** c and d. These profiles indicate that TVs were unaffected by fatigue for both F1 and F2 conditions.
 374 The chemical structure of both substrate and encapsulant layer presented no detectable chemical modification.

375

376 After mechanical fatigue, the studied epoxy resin presented slight stiffening while its other properties
 377 remained unchanged. A stiffening of the PET substrate was similarly accompanied by increases in its
 378 crystallinity but with no change in its chemical structure. These microstructure modifications are probably due
 379 to mechanical effects only. The frequency of mechanical cycles used was probably too low to induce a
 380 substantial rise in the internal temperature by the friction of polymer macromolecules. The chemical structure of
 381 both PET and epoxy resin was also stable under these ageing conditions.

382 TV succumbed to electrical failure under the harshest ageing condition following the formation of cracks
 383 in the glue layer.

384 3.4. Thermo-mechanical coupling

385 All sample types were thermo-mechanical aged. Samples were first aged for 500h at 120°C under air,
 386 followed by mechanical bending for 5 000 cycles on a 50 mm diameter roll (TM1) and finally to 5 000 cycles
 387 on a 25 mm diameter roll (TM2). Mechanical bending cycle experiments were performed at ambient
 388 temperature. Samples characterization used the same techniques as previously described.

389 3.4.1. Epoxy resin TM coupling

390 Analytical characterization of PNE resin was by DMTA, tensile tests and TGA. The results are
 391 summarized in **Table 2**.

392 After ageing under condition TM1, T_g , T_d , and Young's modulus increased. T_β was unchanged. Visual
 393 inspection of the samples revealed a yellowing of the resin. The effect of thermo-mechanical ageing under TM1
 394 condition was the combination of both thermal ageing for at 120°C for 500h and mechanical fatigue under F1
 395 condition. As previously explained for thermal ageing, the simultaneous increase in these parameters reveals
 396 that crosslinking reactions were predominant. Based on the phenomenon of intensity difference between
 397 thermal ageing and mechanical fatigue as previously described, most of the changes observed under the
 398 combined regimen were due to thermal ageing. Yellowing of the resin observed after 500h at 120°C did not
 399 change during the subsequent fatigue.

400 Both T_g and Young's modulus decreased under the harshest (TM2) ageing conditions. An increase in the
 401 effectiveness of chain scission reactions explains this effect.

402

403 As for thermal ageing and fatigue, the β -transition was not affected by thermo-mechanical ageing under
 404 either condition.

405

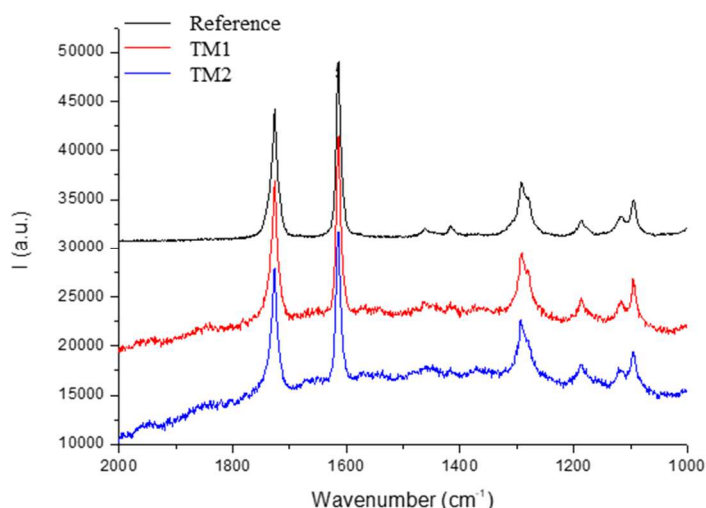
406 A two steps system is identified as underpinning the thermo-mechanical ageing of epoxy resins. The first
 407 step TM1 is the direct addition of thermal ageing and fatigue F1. During this step, the crosslinking reactions
 408 proved dominant as evidenced by the stiffening of the films and increasing of their glass transition temperature.
 409 Yellowing of the resins due to thermal ageing was similarly recorded.

410 The second step TM2 presented different mechanisms, evidenced by a softening of the films and a
 411 decrease in T_g . During this step, chain scission reactions became more competitive.

412 3.4.2. PET substrate TM coupling

413 The changes in thermal and mechanical properties of PET substrates with thermo-mechanical ageing are
 414 presented in **Table 3**. The Young's modulus, strain at break and melting temperature for the PET substrate,
 415 after thermo-mechanical ageing, were not significantly modified under either condition. However, the PET
 416 substrate crystallinity ratio increased slightly. As for the recorded increase in crystallinity after thermal ageing,
 417 this is probably the result of a thermal annealing effect on the film.

418 The Raman spectra of PET films after thermo-mechanical ageing are presented in **Figure 12**. Both the
 419 peak positions and their width were unchanged after ageing, suggesting that the chemical structure of PET was
 420 stable during ageing under these conditions.
 421



422

423 **Figure 12.** Changes in micro-Raman spectra of PET substrate in TVs before and after thermo-mechanical
 424 ageing under TM1 and TM2 conditions

425 Indeed, the mechanical, thermal and chemical properties of the PET films remained stable under
 426 thermo-mechanical ageing.

427 3.4.3. Bilayer and test vehicle TM coupling

428 The PET/PNE bilayer and TV were all subjected to thermo-mechanical ageing. The values of the peeling
 429 force G recorded after ageing are reported in **Table 4**. After ageing under TM1 conditions, the peeling force
 430 increased from 1.74 ± 0.15 N/cm to 2.61 ± 0.19 N/cm. However, this value is of the same magnitude as that
 431 recorded after thermal ageing at 120°C for 500h (2.70 ± 0.14 N/cm), suggests that the recorded increase during
 432 thermos-mechanical ageing TM1 was mainly due to the thermal ageing step. After ageing under condition TM2,
 433 a slight decrease in G was detected. This observation is consistent with the increase in chain-scission efficiency,
 434 evidenced for the epoxy resin ageing under this condition.

435

436 The results of the electrical tests performed on TV are presented in **Table 5**. These tests were positive for
 437 all the chips tested after thermo-mechanical ageing under both conditions. However, the TV aged under the
 438 harshest condition (TM2) presented some delamination between the PET substrate and the encapsulating resin.

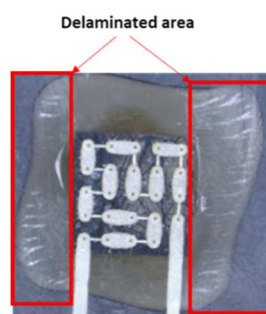
439 Illustrated by the micrograph shown in **Figure 13**, delamination occurred on each side of the silicon chip and
 440 parallel to the bending direction. This is also explained by the stiffening of the resin measured after
 441 thermo-mechanical ageing. Thus conformability of the resin is reduced by this significant stiffening. Stresses
 442 then accumulate at the interface during the bending function of the TV. These observations are different from
 443 those observed for mechanical fatigue under F2 conditions. Here stresses are released when cracks form in the
 444 glue layer. Changes of both polymer materials during the thermo-mechanical ageing lead to modifications in the
 445 distribution of internal stresses that, in turn, results in different release modes.

446 Delamination between resin and substrate enabled water and oxygen to diffuse into the system.
 447 Accordingly, the encapsulation layer ceases to play its protective role. Functional properties would be degraded
 448 with longer ageing periods.

449 **Table 5.** Results of electrical tests performed on TV devices after each ageing condition

<i>Ageing type</i>	Thermal		Fatigue		Thermo-mechanical	
<i>Ageing condition</i>	Reference	500h	F1	F2	TM1	TM2
<i>Electrical test</i>	Positive	Positive	Positive	Negative	Positive	Positive

450



451

452 **Figure 13.** Optical micrograph of a TV after it was subjected to thermo-mechanically ageing under TM2
 453 conditions

454 Micro-Raman depth profiles of TVs, that were thermo-mechanically aged, are presented in **Figure 9** e and
 455 f. As observed after thermal ageing, the micro-Raman depth profiles are dominated by a broad peak for depths
 456 greater than 100 μm when TVs were thermo-mechanically aged. Attributed to the formation of fluorescent
 457 species during thermo-oxidative processes, this peak was nevertheless not modified between TM1 and TM2
 458 conditions.

459 Although yellowing of the epoxy resin developed during the thermal ageing stage, there was no recorded
 460 change during the subsequent mechanical ageing stage.

461 **Conclusion**

462 The durability and functional performances of microelectronic test vehicles comprising epoxy resin
 463 encapsulant and PET substrates have been thoroughly assessed after thermal, mechanical fatigue and
 464 thermo-mechanical ageing. Under moderate (TM1) ageing conditions, the changes observed resulted directly
 465 from combined thermal ageing and mechanical fatigue. Under these ageing conditions, oxidation of the epoxy
 466 resin resulting from the thermal ageing coupled with a stiffening of the films induces an increase of the peeling
 467 force, and reinforcement of the encapsulant/substrate interface. Whereas crosslinking reactions dominated
 468 under moderate ageing TM1 conditions, no further oxidation was detected under harsher TM2 conditions.
 469 Instead, chain scission reactions induced by fatigue stress following thermal ageing (TM2) were dominant. A
 470 softening of the epoxy resin coupled with a decrease in T_g was evidenced. The peeling force required to
 471 decouple the encapsulant from the substrate decreased, and delamination between the encapsulant and the
 472 substrate was observed in TV. While delamination does not always necessarily cause electrical failure, it
 473 probably induces damage to the barrier properties.

474 The peeling tests show that adhesion between the encapsulant and substrate is governed by degradation
 475 mechanisms occurring within the epoxy resin. The failure mechanism of TV as delamination or cracks in the
 476 glue layer is influenced by mechanical changes of all the constituting materials.

477 To that end, if the thermo-mechanical ageing remains inadequately controlled, a variety of reliability
 478 issues, circuit failure, performance degradation, ultimately leading to possible devices damage, will be the
 479 results.
 480

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 485
 486

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