



# Fluorinated epoxy resin as a low adhesive mould for composite material



Patrice Glaris<sup>a,b,c</sup>, Jean-François Coulon<sup>b</sup>, Michel Dorget<sup>a</sup>, Fabienne Poncin-Epaillard<sup>c,\*</sup>

<sup>a</sup>CTTM, rue Thalès de Millet, 72000 Le Mans, France

<sup>b</sup>ECAM Rennes – Louis de Broglie, Campus de Ker Lann – Bruz, 35091 Rennes, France

<sup>c</sup>LUNAM Université, UMR Université du Maine – CNRS no 6283, Institut des Molécules et Matériaux du Mans – Département Polymères, Colloïdes et Interfaces, Avenue Olivier Messiaen, 72085 Le Mans Cedex, France

## ARTICLE INFO

### Article history:

Received 25 October 2013

Received in revised form 26 February 2014

Accepted 31 March 2014

Available online 13 April 2014

### Keywords:

A. Resins

B. Surface properties

D. Surface analysis

D. Mechanical testing

Non-adhesion

## ABSTRACT

The aim of this work is to decrease the adhesion between a cured modified epoxy-based substrate and an in situ cured virgin epoxy-based piece. The effect of perfluorinated additives on the non-adhesion output is investigated through an adapted pull-off test. It appears that additive migration initiates the surface fluorination. Longer the fluorinated chain is, higher the surface fluorination is and weaker the adhesion strength is. The weak chemical affinity between these two epoxy resins is shown to be mainly responsible for these results leading to an adhesive rupture.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

The mould's demoulding behaviour is an economic issue in thermosetting plastic implementation industry. The less adherent the mould is, the higher the number and frequency of production cycles are. In case of further maintenance, cleaning steps of mould and piece surfaces will be reduced. During the injection process of thermosetting plastics, high temperatures are applied in order to cure the piece. However, before a complete curing, the thermosetting plastic goes through a highly reactive intermediary state since the applied curing temperature is higher than its glass transition temperature [1,2]. As a result, the mobility of the growing polymeric chains is strongly increased [3]. For example, kinetics of epoxy resin/diamine systems composed of many reactive species such as ester, hydroxyl, amine and oxirane groups is controlled by diffusion process during this intermediate state [2,4–6]. Thus, these reactive species can migrate towards the mould/piece interface and promote chemical bonding leading to adhesion at the interface [7,8]. Moreover, such adhesion phenomena might be strongly increased in case of epoxy resin-based mould since autohesion between uncured and cured epoxy resin could also occur [9]. Therefore, the surface of epoxy resin-based moulds needs specific treatment in order to limit their adhesion to the piece. Fluorinated polymers such as polytetrafluoroethylene (PTFE) are

well-known for their very low surface energy leading to low adhesive properties mainly due to their chemical composition and specially to C–F bonds which are stronger and shorter than C–H ones [10–12]. To mimic such surface properties, surface fluorination with perfluorinated adducts was shown to be an efficient way to reduce surface energy [13,14]. This method was successfully applied to decrease the surface energy of cured epoxy resins [15–17]. However, to our knowledge, adhesion properties of such modified epoxy resins had never been evaluated before. Thus in the present work, a DGEBA (diglycidyl ether of bisphenol A) type epoxy resin was modified with different perfluorinated additives before to be cured with an amine-type curing agent. Final surface physicochemistry was first determined through contact angle and X-ray Photoelectron Spectroscopy (XPS) measurements. Then, practical adhesion between this cured modified epoxy resin and an in situ cured virgin epoxy resin was measured through an adapted pull-off test. Adhesion results are discussed in terms of free surface energy of the modified epoxy resins, chemical affinity between the 2 resins and also mechanical properties of final surface of cured modified epoxy resins.

## 2. Materials and methods

### 2.1. Chemical compounds

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin Polylox E064 (purity 100%) was supplied by Dow Chemicals

\* Corresponding author. Tel.: +33 243832698.

E-mail address: [fabienne.poncin-epaillard@univ-lemans.fr](mailto:fabienne.poncin-epaillard@univ-lemans.fr) (F. Poncin-Epaillard).

(Germany). An aromatic diamine: the 4,4'-methylenebis(2,6-diethylaniline) (MDEA, purity >99%) supplied by Lonza (Switzerland) was used as the curing agent. Three perfluorinated acids: perfluoroheptanoic acid (F13), perfluorononanoic acid (F17) and perfluorododecanoic acid (F23) were supplied by Aldrich (France). All products were used as received.

## 2.2. Substrate preparation

Virgin epoxy resin (EM) was synthesised by mixing a 70/30 DGEBA/MDEA weight ratio. Curing was done at 180 °C during 2 h.

Fluorinated epoxy resins were synthesised by first mixing the perfluorinated acid and the DGEBA leading to the formation of an ester [15,18]. Then, a stoichiometric amount of curing agent (MDEA) relatively to that of DGEBA is added and the whole blend is cured 2 h at 180 °C to perform complete curing of DGEBA.

For mechanical study, the curing is done in presence of a polytetrafluoroethylene (PTFE) stamp. According to Lavielle et al. [19], polymeric molecules conformation does not depend on the interface nature (EM/air or EM/PTFE). Further confirmation was given by contact angle values which were found to be similar whatever the interface.

## 2.3. Surface analysis

Surface physicochemistry was investigated through contact angle measurement. Contact angle of 5  $\mu$ L drops of water (wCA), diiodomethane (dCA) and virgin epoxy resin (EMCA), were measured using the sessile drop technique. Measurements were done with a Ramé–Hart 100-00-230 goniometer once samples were cooled to ambient temperature. For each sample, 10 measurements were performed. Owens–Wendt method was then used to calculate the free surface energy ( $\gamma_s$ ) of the cured resins.

The surface chemical composition of substrates was investigated by X-ray photoelectron spectroscopy (XPS). XPS spectra were collected with an Axis Nova X-ray photoelectron spectrometer from Kratos Analytical (Manchester, UK). XPS measurements were performed with a Mg K $\alpha$  X-ray source at 15 kV and 20 mA emission. Charge neutralization was applied during sample analysis. Emission angle of photoelectron was 90° which approximately corresponds to a penetration depth of 9 nm [16]. Spectra decomposition was realised thanks to Casa XPS software.

## 2.4. Adaptation of geometry for pull-off test with injected thermosetting plastics

The main difficulty with flat substrates is to ensure reproducible spreading of the epoxy resin over the tested substrate. Another possibility is to explore the ISO 4624: 2002 standard that advises of cutting the resin around dolly sides [20]. However, since the cured RTM6 is a fragile material, failures occurred while cutting and propagated during the pull-off test thus promoting a cohesive rupture of the piece. Using a metallic ring for avoiding the resin spreading has been also tried but leaks may still occur.

Therefore, the chosen solution was to replace the flat substrate by one bearing a cavity as represented in Fig. 1. This type of geometry completely avoids the uncured epoxy resin spreading. Moreover, contact area between the epoxy resin and the substrate is easily controllable with the volume of the resin poured in the cavity. The nature of the stress applied during the pull-off test also depends on the cavity shape but, because of its continuous shape, a hemispherical cavity ensures a pure tensile stress while a square shaped cavity induces 2 types of solicitation: tensile stress at horizontal piece/substrate interface and shear stress at vertical piece/substrate interface. Just note that other cavity geometries,

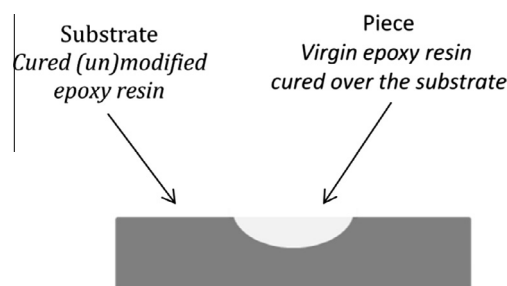


Fig. 1. Schema of substrate bearing a hemispherical cavity poured with liquid epoxy resin afterward cured.

like those with reducing section from the top to the bottom could be used but they are less convenient for this test.

Pull-off test was carried out with an Instron 4204 tensile tester equipped with a 50,000 N strength cell. An adapted assembly was developed to insert and hold an aluminium dolly glued to EM pieces inside the tensile tester while substrates were held by two aluminium rods at the bottom. Aluminium rods were placed as closed as possible from the tested area in order to prevent torsions in the substrate while pulling off the EM piece. 12 mm diameter aluminium dollies were glued to the epoxy piece thanks to an epoxy adhesive (Araldite 2011, bi-component resin supplied by Huntsman – Switzerland). According to the supplier, Araldite 2011 lap shear strength is up to 21.5 MPa while cured one hour at 70 °C. At the top of this assembly, a 14 mm diameter ball joint supplied by Mycelium Roulement (France) allows the system to freely rotate on each axis. Ultimate tensile strength supported by the ball joint, (16 kN as indicated by the supplier) is widely sized to our study whose strengths did not exceed 3000 N. Test speed was kept constant at 3 mm/min throughout the experiments. 14 mm diameter cavity was used for the substrate in order to obtain good repartition of stress and to minimize cohesive ruptures in the piece due to its torsion.

## 3. Results and discussion

### 3.1. Surface properties of an epoxy resin modified with perfluorinated additives (EMF)

#### 3.1.1. Wettability properties

Surface physicochemistry of both pristine and modified cured epoxy resins was first investigated through contact angles (CA) measurement. Fig. 2 shows how water and diiodomethane contact angles evolve against additive concentration in the bulk. A little additive concentration allows increasing both water and diiodomethane contact angle values at the surface of cured material. As an example, 1 wt% of F13 leads to wCA and dCA increase, respectively from 70° to 85° and from 28° to 42°. Whatever the additive used, curves shapes were found to be similar for both liquids: CA values increase until a plateau is reached. This plateau occurs earlier for epoxy resin modified with F23 ( $\approx$ 2 wt%) than for epoxy resins modified with F17 ( $\approx$ 3 wt%) and F13 ( $\approx$ 4 wt%). The bigger is the fluorinated additive, the lower the concentration required observing maximum wCA and dCA is [21–23].

Moreover, it appears that the increase of CA values depends on the molecular weight of the additive, respectively higher with F23 > F17 > F13 (Table 1). Maximum surface energy ( $\gamma_s$ ) obtained for each additive was determined (Table 1). As expected,  $\gamma_s$  decreases when epoxy resin composition is modified with a fluorinated additive and this decrease is higher in presence of F23 as predicted by CA values. With this latter case, its surface energy is lower than that of PTFE showing its low adhesive properties. The

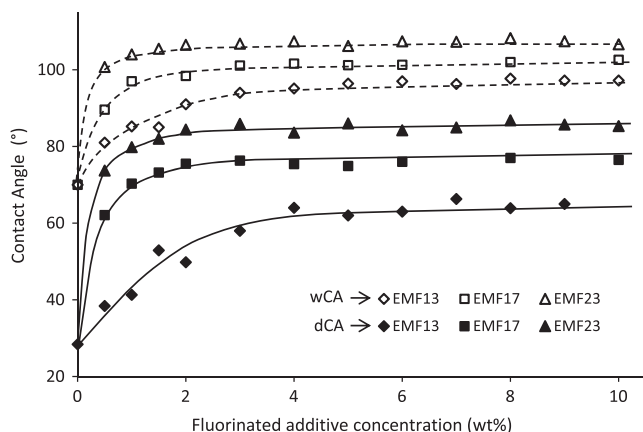


Fig. 2. Water (empty marks) and diiodomethane (full marks) contact angle evolution versus concentration of fluorinated additive in modified epoxy resins.

Table 1  
Maximum contact angle values and surface energies of cured epoxy resins modified with perfluorinated additive.

Formulation	$\theta_{\text{Water}} (^{\circ})$	$\theta_{\text{Diiodomethane}} (^{\circ})$	$\gamma_s (\text{mJ m}^{-2})$
EM	75.4 ± 1.2	28.4 ± 1.2	45 ± 2
EMF13	97.5 ± 1.1	64.0 ± 1.5	26 ± 2
EMF17	101.6 ± 1.1	75.0 ± 1.7	22 ± 2
EMF23	106.5 ± 1.3	84.5 ± 1.5	15 ± 2
PTFE	103.5 ± 1.5	76.0 ± 1.2	19 ± 2

hypothesis of a migration of fluorinated additive towards air/solid interface during the epoxy resin curing in order to minimize free surface energy of final material is often proposed to explain such surface properties, however, with few experimental data on such phenomenon in the case of epoxy matrices [15,16].

### 3.1.2. Surface chemical composition

XPS analysis of EM was performed as reference (Fig. 3). XPS spectrum revealed that oxygen (O1s), nitrogen (N1s) and carbon

Table 2  
Theoretical (Th) and experimental elements proportions (XPS) at surface of virgin and modified epoxy resins.

	O1s (%)		N1s (%)		C1s (%)		F1s (%)	
	Th	XPS	Th	XPS	Th	XPS	Th	XPS
EM	12.3	11.2	2.7	2.7	85.0	86.1	–	–
EMF13		12.0		1.6		78.4		10.0
EMF17	11.0	11.6	2.5	1.0	84.5	71.0	2.0	16.4
EMF23		8.0		<1.0		55.8		36.2

(C1s) mainly composed the extreme surface of EM. Their proportions are respectively of 11.2%, 2.7% and 86.1% and are coherent with theoretical ones (Table 2). High resolution C1s spectrum (Fig. 3b) revealed that carbon is linked to oxygen and nitrogen by simple bonds (peak at 286.4 eV) and to other carbon atoms by both simple (285 eV) and double (284.5 eV) bonds [24]. High resolution O1s spectrum (Fig. 3c) shows 2 substructures at 532.4 and 533 eV respectively characteristic of C–OH and C–O–C bonds. Evidence of C–OH bonds confirms the epoxy ring scission. All these structures are related to DGEBA and MDEA molecules. Moreover, their proportions, determined from XPS spectra, were found to be similar than theoretical ones for bulk composition (Table 2), indicating that EM has a homogeneous composition after curing.

XPS spectrum of epoxy resins modified with 4 wt% of F17 (Fig. 4) presents a peak at 689 eV characteristic of fluorine (F1s) whose proportion is higher than expected theoretical value (16.4% at the extreme surface of EMF17 against 2% for a homogeneous composition of cured EMF17, Table 2). C1s high resolution spectrum (Fig. 4b) shows peaks at 291.8 and 294 eV, respectively assigned to CF<sub>2</sub> and CF<sub>3</sub> groups which belong to F17 in a higher proportion than that predicted (8.5% instead of 0.9% for CF<sub>2</sub> and 1% instead of 0.1% for CF<sub>3</sub>, Table 3). Therefore, one may conclude to EMF17 surface enrichment in fluorinated additive during its curing. O1s high resolution spectrum of EMF17 (Fig. 4c) also presents differences in comparison to that of EM surface. Instead of 2 substructures, 4 ones are observed and assigned to chemical functions of EM (C–OH at 532.9 eV, C–O–C at 533.3 eV) and ester bonding between DGEBA and F172 (O–CO at 532.2, and O–CO at 534.5 eV, Table 4).

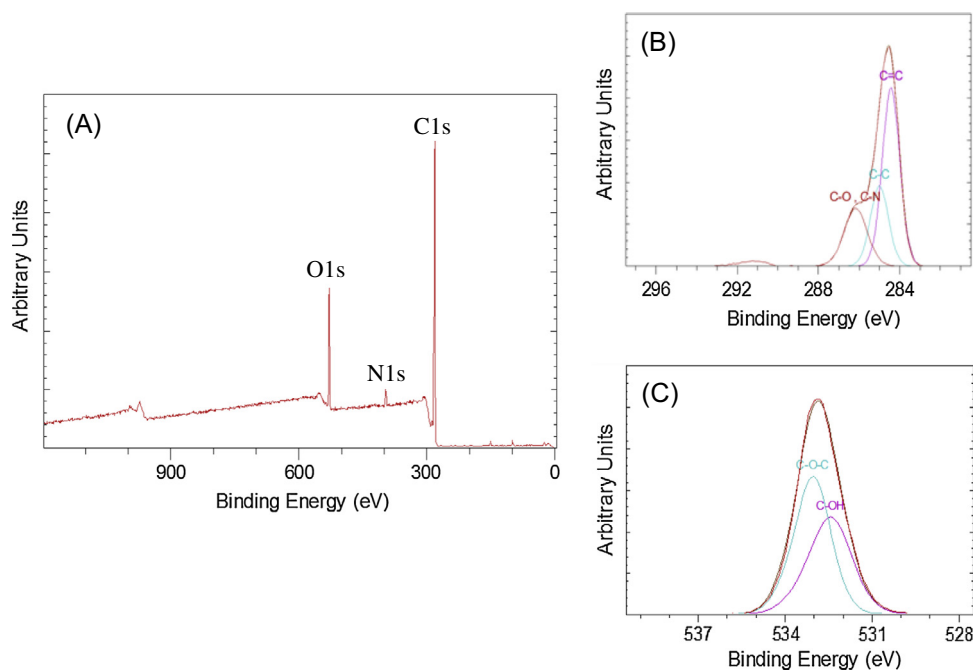


Fig. 3. XPS (A) survey spectrum, (B) C1s high resolution and (C) O1s high resolution spectra of EM surface.

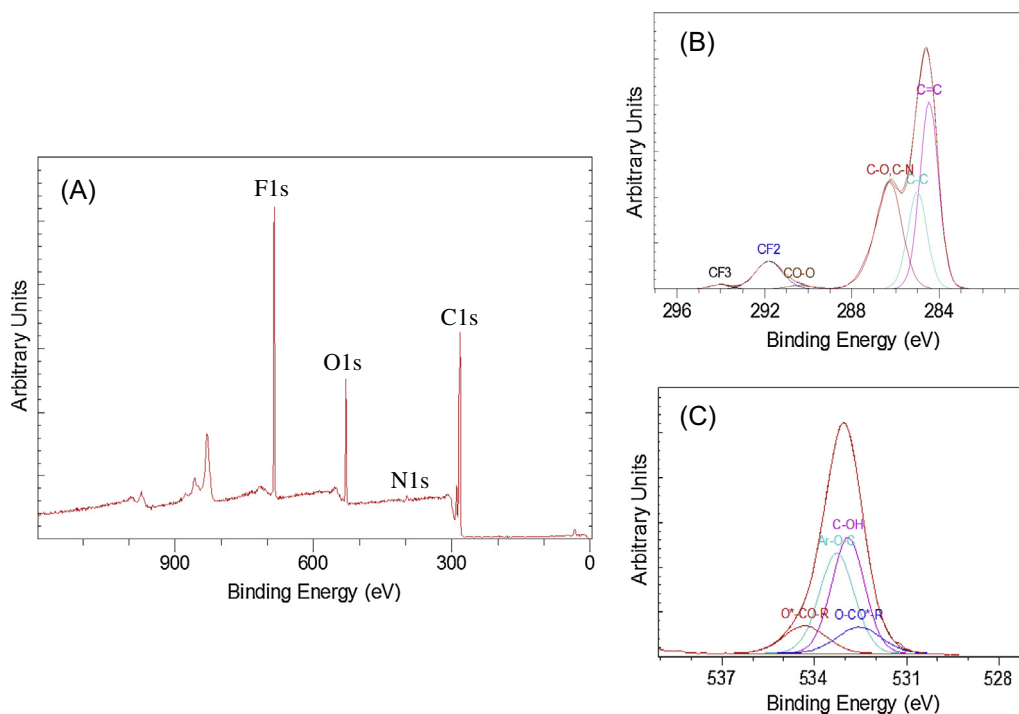


Fig. 4. XPS: (A) survey spectrum, (B) C1s high resolved spectrum and (C) O1s high resolved spectrum of EMF17 surface.

Table 3

Carbon (C1s) and oxygen (O1s) substructures proportions determined by XPS of the surface of epoxy resins modified with different fluorinated additives.

	C1s						O1s				DGEBA-Fx Th (%)	XPS (%)
	C=C (%)	C-C (%)	C-O/C-N (%)	CO-O (%)	CF <sub>2</sub> (%)	CF <sub>3</sub> (%)	φ-O-C (%)	C-OH (%)	O-CO (%)	O-CO (%)		
EMF13	41.0	20.5	32.3	0.4	5.4	0.4	41.7	37.5	10.4	10.4	5.6	50
EMF17	38.8	21.6	29.1	1.0	8.5	1.0	39.6	35.6	12.4	12.4	4.4	63
EMF23	26.5	14.7	24.7	3.9	25.8	3.9	35.2	29.6	17.6	17.6	3.3	100

Similar XPS analyses were done for resins modified with 4 wt% of F13 (EMF13) and F23 (EMF23). Tables 2 and 3 summarize all data. It can be pointed out that atomic fluorine concentration at the extreme surface of modified epoxy resins is higher when the additive molecular weight increases. It grows from 10.0% for an epoxy resin modified with F13 to 36.2% for an epoxy resin modified with F23. Beside, when the additive size increases, the proportion of non-fluorinated groups (C=C; C-C; C-O; C-N) decreases whereas that of fluorinated groups (CF<sub>2</sub>; CF<sub>3</sub>) increases (Table 3). The proportion of perfluorinated additive linked to a DGEBA molecule (DGEBA-Fx bond) can be obtained from O1s high resolution spectrum (Table 4) if assuming that φ-O-C bonds are representative of such addition and if its proportion is proportional to that of DGEBA (%DGEBA = (%φ-O-C)/2). Then, the DGEBA-Fx bond ratio can be determined by the relation (1):

$$(\%)DGEBA - Fx = \frac{O - CO}{\left(\frac{1}{2}\right) * (\phi - O - C)} \quad (1)$$

As observed, DGEBA-Fx bond proportion at the extreme surface of modified epoxy resins is quite far from theoretical predictions. The experimental ratio varies from 50% to 100% instead less than 6% for theoretical values. Moreover, it appears that DGEBA-Fx bond proportion in function of additive size varies in an opposite manner from theoretical predictions. Additive superficial concentration of modified epoxy resin is higher when a bigger additive is used. By combining results of Tables 2 and 3, structural hypothesis of the

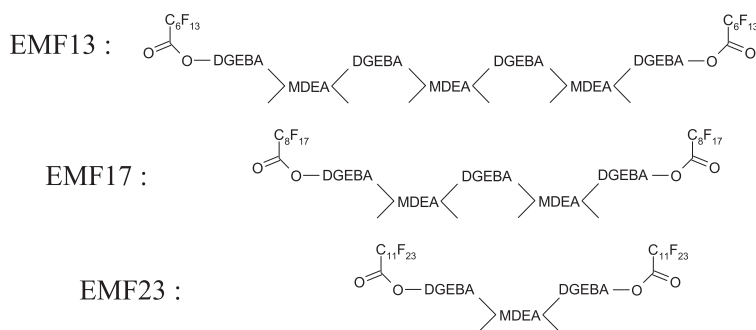
surface can be drawn (Table 4). These chemical structures reveal the presence of a composite surface where perfluorinated chains could be separated by DGEBA-MDEA molecules. The bigger is the additive; the lower is the space between perfluorinated chains at the surface of the modified epoxy resin. This leads to the conclusion that surface fluorination of a modified epoxy resin is governed by two features. The first one is final perfluorinated additive density at the surface which is consequent with high molecular weight additives. The second one is that a bigger perfluorinated additive at surface leads to more fluorinated groups, even if the experiments were carried out at constant fluorine concentration. The combination of these 2 aspects leads to high fluorinated surfaces with low surface energy.

### 3.2. Interfacial properties between two epoxy resins

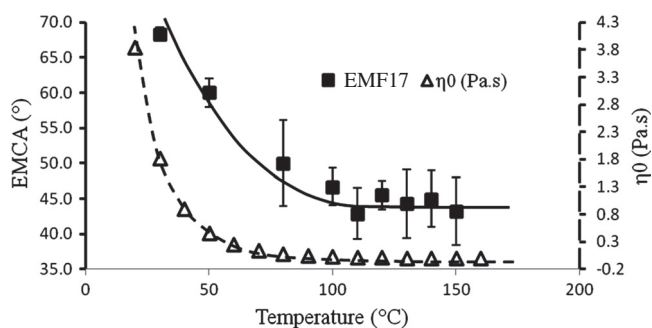
#### 3.2.1. Wetting of a cured epoxy resin modified with fluorinated additive (EMF) by a virgin epoxy resin (EM)

Interfacial properties between two epoxy resins were first investigated through contact angle measurements at different temperatures (from 25 to 150 °C) of a virgin epoxy resin onto cured modified epoxy resins (Fig. 5). Contact angle of epoxy resin EM, so called EMCA, deposited onto cured EMF17 decreases with temperature until a plateau (EMCA = 45.5°) is reached for temperatures exceeding 90 °C. These wetting results can be related to evolution of EM initial viscosity ( $\eta_0$ ) against temperature. Further, the EMCA

**Table 4**  
Hypothesis on the chemical structure of modified epoxy resins surface and its associated theoretical elements proportions.



Resin	C (%)	N (%)	O (%)	F (%)
EMF13	75.6	2.8	9.4	12.2
EMF17	70.2	2.3	8	19
EMF23	55	1.4	8.8	34



**Fig. 5.** EMCA onto EMF17 (full squares) and EM initial viscosity (empty triangles) versus temperature.

at the plateau must be interpreted as an equilibrium contact angle which occurs when EM viscosity is low enough for a complete spreading of the drop onto the substrate.

At ambient temperature (25 °C), EM drop wetting is weaker for EMF substrates ( $\theta = 55^\circ$  onto EMF13 and  $\theta = 68^\circ$  onto EMF23) than for EM one ( $\theta = 23^\circ$ ) (Table 5). In a similar manner, EM wetting is lower for lower surface energy substrates, related to the extreme surface fluorination described before. As a result, the affinity between the two resins decreases resulting in lower EM wetting, phenomenon more pronounced with high molecular weight perfluorinated additives.

At 120 °C, EMCA becomes almost negligible showing a complete wetting of EM substrate. At this temperature, EMCA shows a slighter decrease onto EMF substrates which not exceed at least 38°. It must be pointed out that, EM wetting onto PTFE substrate ( $\theta = 70^\circ$ ) is lower than onto EMF23 substrate ( $\theta = 50.5^\circ$ ). Since the latter

**Table 5**  
Surface energy, contact angle and associated  $1 + \cos(\theta)$  value of a 5  $\mu$ L EM drop, for various substrates at ambient and curing temperatures.

	25 °C			120 °C	
	$\gamma_s$ (mJ m <sup>-2</sup> )	EMCA (°)	$1 + \cos(\theta)$	EMCA (°)	$1 + \cos(\theta)$
EM	45 ± 2	23 ± 3	1.92	≈0	2.00
EMF13	26 ± 3	55 ± 1	1.57	38 ± 1.4	1.78
EMF17	21 ± 1	62 ± 3	1.47	45 ± 2	1.71
EMF23	15 ± 2	68 ± 2	1.37	50 ± 2	1.64
PTFE	19 ± 2	76 ± 2	1.24	70 ± 2	1.34

presents a lower surface energy than the former, opposite results were expected leading to the conclusion that surface energy is not the main criteria. These differences may be explained by the surface chemical composition and its homogeneity. All the surface characterisation of EMF23 tend us to conclude to a heterogeneous and composite chemical structure while PTFE surface, less thermal sensitive material, should have a more homogeneous chemical nature and therefore with weaker affinity towards EM.

### 3.2.2. Determination of interfacial properties between two epoxy resins thanks to mechanical testing

Fig. 6 shows the strength variation versus the elongation for piece/substrate couples referred as EM/EM (6a) and EM/EMF13 (6b). On both figures, two main areas are observed. In the first one, the whole system (piece + substrate) is under tension. In this step, the first increase in measured strengths up to 50 N ± 7 N characterizes the first contact between aluminium rods and the substrate. A plateau is then observed which corresponds to contact equilibrating between aluminium rods and the substrate. In the second area, the measured strength increases until rupture occurs in the system. The strength linear increase indicates that no plastic deformation occurs during the test [25]. The slope characterising the elastic deformation of tested system was found to be the same for each sample (10.7 ± 0.7 kN/mm). This signifies that whatever the tested substrate, the elastic deformation induced by tensile stress is the same. These mechanical behaviour reflects rigid (high slope value) and brittle (no plastic deformation) behaviour of cured epoxy resins [26]. Rupture in piece/mould assembly is characterized by the sudden drop of strength values so that maximum strength value of curves corresponds to the ultimate tensile strength needed to break the assembly.

Measured strength and type of rupture for each piece/substrate couple are presented in Table 6. In case of an EM substrate, only cohesive rupture is observed for strength sometimes higher than 2000 N. At the opposite, modification of substrate chemical composition with a perfluorinated additive leads to adhesive ruptures only. It interesting to observe that needed strength to observe these adhesive ruptures decrease while a bigger additive is used. However, this phenomenon does not seem to be only linked to physicochemical properties of substrates. In fact, it appears that no linear relation is found between substrate surface energy and adhesive strength (Table 6). Measured strength decreases from 1750 to 320 N when modifying the substrate epoxy resin with F17. However, for an EMF23 based substrate which has lower

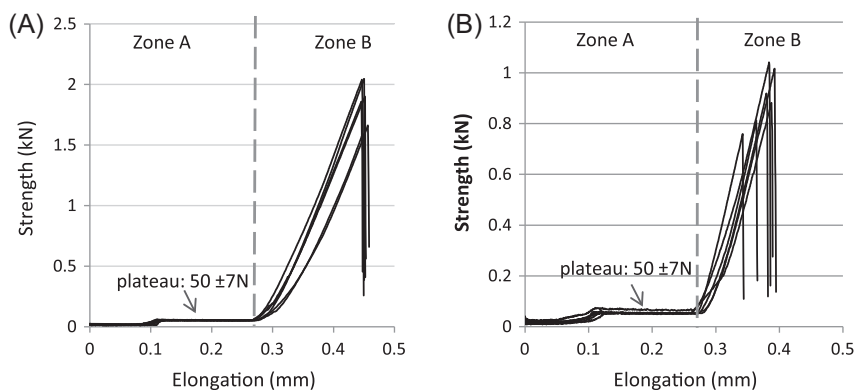


Fig. 6. Types of curves issued from pull-off test realised for EM/EM (A) and EM/EMF13 (B) piece/substrate assemblies.

Table 6

Type of rupture and associated strength observed for pull-off testing of different piece/substrate assemblies.

Mould composition	Surface energy ( $\text{mJ m}^{-2}$ )	$1 + \cos(\theta)$ at 120 °C	Ultimate tensile strength (N)	Rupture type
EM	$45 \pm 2$	2	$1750 \pm 370$	Cohesive
EMF13	$26.3 \pm 2$	1.78	$920 \pm 160$	Adhesive
EMF17	$21.6 \pm 2$	1.71	$320 \pm 40$	Adhesive
EMF23	$16 \pm 2$	1.64	$410 \pm 65$	Adhesive

surface energy than an EMF17 based one, no decrease of adhesive strength is observed while a smaller value was expected. Since study of substrates wetting by EM reveals that less affinity is obtained while substrate epoxy resin is modified with bigger additive, it is clear that other phenomena leads to the observed behaviour of EMF23 substrate. The first one could be a fluoroalkyl chains crystallization and the second could be based on thermo-mechanical properties. These properties of the extreme surface of EMF23 substrate may be at the origin of such behaviour. In fact, nature of polymer end groups has been shown to lead to surface properties different from bulk ones by Kajiyama et al. [27,28]. As an example, for perfluorinated poly(2-vinylpyridine) in which surface chemistry differs from bulk one due to migration of fluorinated species, they showed with Atomic Force Microscopy analysis that surface glass transition temperature is lower than that of the bulk [27]. Excess free volume at extreme surface due to the huge amount of shorter polymer chains is responsible for this phenomenon according to the authors. Here, the modified epoxy resins exhibit highly chemical difference between the bulk and the extreme surface due to perfluorinated end epoxy chains. As shown before, the bigger is the additive, the bigger is the density of such end chains at extreme surface and as a consequence, the higher is the excess free volume. This may lead to various interphases depending on the type of perfluorinated which is used. For EMF23, beside the fluoroalkyl crystallization, this interphase possesses a less rigid behaviour and as a consequence promotes energy dispersion during the tensile test.

#### 4. Conclusions

This study reveals how adhesion of cured epoxy resins can be lowered through its modification with perfluorinated additive. Additive migration towards air/resin interface leads to high fluorination of the final cured epoxy resin surface which is responsible for high decrease of final material surface energy. Surface fluorine concentration is shown to be related to additive perfluorinated chain length: the longer is, the higher its surface concentration in

the cured state is. As a result, affinity between such surfaces and an uncured epoxy resin is highly decreased. Mechanical testing of the epoxy–epoxy interface was then performed thanks to an adapted pull-off test. It appears that perfluorinated epoxy resins lead to adhesive rupture while only cohesive ruptures are obtained with non modified resin. Since these adhesive strengths are lower and lower while using a longer additive, we assumed that low affinity between the substrate and the uncured resin was responsible of strength lowering. However, some irregularities in strength evolution pointed out that the mechanical properties of extreme surface also evolve with additive length. In fact, the higher is the surface density of fluorinated additive, the higher is the excess free volume at extreme surface. This effect is shown to counterbalance adhesive strength reduction due to affinity lowering.

#### References

- [1] Pascault JP, Sautereau H, Verdu J, Williams RJJ. *Thermosetting polymers*. Taylor & Francis; 2002.
- [2] Barrère C, Maso FD. Résines époxy réticulées par des polyamines: structure et propriétés. *Revue de l'Institut français du pétrole* 1997;52:317–35.
- [3] De Gennes PG. In: *Scaling concepts in polymers physics*. Cornell University; 1979.
- [4] Lee H, Neville K. *Handbook of epoxy resins*. McGraw-Hill; 1967.
- [5] Tillet G, Bernard B, Bruno A. Chemical reactions of polymer crosslinking and post-crosslinking at room and medium temperature. *Prog Polym Sci* 2011;36:191–217.
- [6] Paul S. *Surface coatings: science & technology*. 2nd ed. John Wiley & Sons; 1996.
- [7] Lee LH. *Fundamentals of adhesion*. Plenum Press; 1991.
- [8] Prolongo SG, Rosario GD, Urena A. Comparative study on the adhesive properties of different epoxy resins. *Int J Adhes Adhes* 2006;26:125–32.
- [9] Kinloch AJ. *The science of adhesion*. Part. 1. Surface and interfacial aspects. *J Mater Sci* 1980;15:2141–66.
- [10] Ameduri B, Boutevin B. *Well-architected fluoropolymers – synthesis, properties and applications*. Elsevier; 2004.
- [11] Bonnet JF, Tournut C. *Techniques de l'ingénieur*, 1990, AM 3390.
- [12] Simons JH. *Fluorine chemistry*. Academic Press; 1964.
- [13] Fox HW, Zisman WA. The spreading of liquids on low-energy surfaces. II. Modified tetrafluoroethylene polymers. *J Colloid Sci* 1952;7:109–21.
- [14] Schulman F, Zisman WA. The spreading of liquids on low-energy surfaces. V. Perfluorodecanoic acid monolayers. *J Colloid Sci* 1952;7:465–81.
- [15] Miccio LA, Fasce DP, Schreiner WH, Montemartini PE, Oyanguren PA. Influence of fluorinated acids bonding on surface properties of crosslinked epoxy-based polymers. *Eur Polym J* 2010;46:744–53.
- [16] van de Grampel RD, Ming W, van Gennip WJH, van der Velden F, Laven J, Niemantsverdriet JW, et al. Thermally cured low surface-tension epoxy films. *Polymer* 2005;46:10531–7.
- [17] Matuszczak S, Feast WJ. An approach to fluorinated surface coatings via photoinitiated cationic cross-linking of mixed epoxy and fluoroepoxy systems. *J Fluorine Chem* 2000;102:269–77.
- [18] Matejka L, Pokorny S, Dusek K. Network formation involving epoxide and carbonyl groups. *Polym Bull* 1982;7:123–8.
- [19] Lavielle L, Sanfeld A, Schultz J. Orientation thermodynamics at polymer–liquid interfaces. In: *Capillarity Today*, Brussels (Belgium) 1990.
- [20] *Paints and varnishes – Pull-off test for adhesion*. ISO 4624. 2002.
- [21] Ameduri B, Bongiovanni R, Malucelli G, Pollicino A, Priola A. New fluorinated acrylic monomers for the surface modification of UV-curable systems. *J Polym Sci Part A: Polym Chem* 1999;37:77–87.

- [22] Sangermano M, Bongiovanni R, Priola A, Pospiech D. Fluorinated alcohols as surface-active agents in cationic photopolymerization of epoxy monomers. *J Polym Sci Part A: Polym Chem* 2005;43:4144–50.
- [23] Sangermano M, Bongiovanni R, Malucelli G, Priola A, Pollicino A, Recca A. Fluorinated epoxides as surface modifying agents of UV-curable systems. *J Appl Polym Sci* 2003;89(6):1524–9.
- [24] Briggs DJ. High resolution XPS of organic polymers: the Scienta ESCA300 database. John Wiley & Sons; 1992.
- [25] François D. Essais mécaniques et lois de comportement. Hermès, 2001.
- [26] Bardonnnet P. *Techniques de l'ingénieur*, 1992, A 3465.
- [27] Jiang X, Yang CZ, Tanaka K, Takahara A, Kajiyama T. Effect of chain end group on surface glass transition temperature of thin polymer film. *Phys Lett A* 2001;281:363–7.
- [28] Tanaka K, Jiang X, Nakamura K, Takahara A, Kajiyama T. Effect of chain end chemistry on surface molecular motion of polystyrene films. *Macromolecules* 1998;31:5148–9.