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Influence of the chemical composition and formulation of fluorinated epoxy resin on its surface characteristics

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ABSTRACT

The incorporation of perfluorononanoic acid into epoxy resins was investigated in order to prepare a material with low adhesion properties (low free surface energies comprised between 15 and 26 $\mathrm{mJ\,m^{-2}}$). A laboratory-grade tetrafunctional epoxy resin was fluorinated by direct reaction with the perfluorinated carboxylic acid. A bifunctional epoxy resin fluorinated beforehand was also added to the tetrafunctional epoxy resin. The fluorinated resins were analyzed by FTIR spectroscopy. Dynamic DSC experiments were performed for the resins in presence of a stoichiometric quantity of the curing agent. Results were compared with those obtained with a commercial grade of the fluorinated tetrafunctional resin. Finally, the influence of the curing cycle was studied and optimized. The surface properties of the cured resins were then characterized in terms of free surface energy with contact angle measurements.

1. Introduction

Epoxy resins are widespread in a broad range of applications, such as coatings [1,2], adhesives [3,4] and fiber-reinforced composites mainly for the aerospace industry [5–7]. Depending on their application, specific surface properties such as chemical stability or affinity, high thermal stability, improved tribological properties, adhesion or non-adhesion properties, can be required. The hydrophilic properties of epoxy resins are sought after for specific applications such as the reduction of the protein adsorption in capillary zone electrophoresis [8] or to prevent the tissue calcification on bioprosthetic heart valves [9]. However, important researches were mainly carried out to improve the hydrophobic properties of epoxy resins. Since the initial works of Griffith [10], the fluorination of such resins remains highly active [11–14]. One option is to directly fluorinate the epoxy resin before curing and then to cure it pure or mixed with a pristine epoxy resin. Another possibility consists of curing the pristine epoxy resin with a fluorinated curing agent. Among the different fluoro-molecules described, we can cite the perfluoro acid chloride [15], the piperazine and the morpholine derivatives [16], the 4-chlorobenzotrifluoride [17], the laurylfluoro-1-pentanol [18] and the trifluoromethyl aniline [19]. However, the perfluoro carboxylic acid [11–13] remains more commonly encountered and the DGEBA was certainly the most studied epoxy resin. The incorporation of perfluorinated additives into an epoxy resin formulation for producing a material with low adhesion properties was proposed [12]. The authors compared the influence of 3 linear perfluorinated carboxylic acids with different chain lengths and covalently bonded to an epoxy resin, on the surface properties of the cured material, depending on the initial additive concentration. The diffusion of the perfluoroalkyl groups towards the air-resin interface during the resin curing led to high fluorine proportions at the surface (up to 34 mol%), and consequently to low free surface energies (15–26 $\mathrm{mJ\,m^{-2}}$), similar to the ones of fluorinated polymers such as polytetrafluoroethylene (PTFE; $\sim$19 $\mathrm{mJ\,m^{-2}}$). Glaris et al. [13] also showed that the diffusion rate of the perfluoroalkyl groups was dependent on the curing temperature of the resin, and suggested a competition between 2 distinct phenomena. In one hand, the viscosity reduction caused by the temperature increase tends to accelerate the diffusion rate; on the other hand, the increase of the curing kinetic, leading to the reduction of the gelation time, limits this diffusion.

Musto et al. [20] studied the mechanism and the curing kinetics of a commercial tetraglycidylmethylenedianiline (TGDDM) mixed with a perfluoro ether oligomer cured with the methyl nadic anhydride whereas Ragosta et al. [21] studied the mechanical properties of the same system. More recently, Rolere et al. [10] fully investigated the influence of the curing temperature on the diffusion rate of the perfluorinated chains towards both interfaces (air-resin and substrate-resin) of such a modified commercial epoxy resin. This diffusion was

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shown to be highly dependent on the curing temperature, and was found optimal between 70 °C and 110 °C with a fluorine/carbon ratio of 0.59 at the air-resin interface. Curing such a resin at higher temperature led to a lower surface fluorination and finally, a two-step curing (first step at 70 °C followed by a second one at a higher temperature, i.e. 170 °C) was suggested in order to optimize the diffusion and consequently the surface fluorination. It should be noted here, that the surface fluorination means here chemical processes (i.e. fluorination and formulation) allowing the alteration and the control of the surface characteristics of the cured resin.

Thus, the main objective of this study was to investigate the influence of the multi-step curing process on the surface energy of fluorinated laboratory grade TGDDM based resin formulations. Different fluorination routes were also investigated and characterized in terms of composition with FTIR spectroscopy. The non-isothermal DSC was performed to assess the impact of the fluorination on the curing kinetics. The surface properties of the cured resins were characterized in terms of free surface energy through contact angle measurements.

2. Experimental

2.1. Materials

Two liquid epoxy resins were used: (1) the tetra-functionalized epoxy molecule named “Tetra”, composed of tetraglycidylmethylenedianiline (TGDDM), with a theoretical epoxy equivalent weight (EEW) of 105.6 g eq^{-1}, and a surface tension $\gamma = 66.4\ \mathrm{mJ\,m^{-2}}$ [22]; (2) the bi-functionalized epoxy molecule named “Bi”, composed of 2,2’-(butane-1,4-diylbis(oxymethylene))dioxirane (theoretical EEW = 101.12 g eq^{-1},$\gamma = 43.0\ \mathrm{mJ\,m^{-2}}$ [23]). The hardener was 4,4′-methylenebis(2-methylcyclohexylamine), with a theoretical amine hydrogen equivalent weight (AHEW) of 59.6 g eq^{-1}, and $\gamma = 33.7\ \mathrm{mJ\,m^{-2}}$. Perfluorononanoic acid named “F” ($\gamma = 16.6\ \mathrm{mJ\,m^{-2}}$) was selected for the fluorination of the epoxy resins, based on the previous works [12–14]. All chemicals were supplied by Sigma-Aldrich (France) and used as received. The EPOLAM 2090 commercial grade resin (Axson North America, Inc) was used as a reference.

2.2. Sample preparation

2.2.1. Epoxy resin formulation

2.2.1.1. Preparation of the uncured TetraF. A beaker of pure Tetra was partially immersed in a water bath and the temperature was set at 80 ± 5 °C to reduce its viscosity. The quantity of F added to Tetra was chosen to represent 4% of the total weight (Tetra + F + Hardener), as recommended by Glaris et al. for a DGEBA/MDEA mixture [12]. The esterification between the carboxylic group of the fluorinated acid (F) and the resin epoxide group led to the formation of an uncured fluorine-grafted epoxy resin. The mixture was magnetically stirred until the obtention of a homogeneous brown compound.

2.2.1.2. Preparation of the uncured (TetraBi)F. Tetra-functionalized resin is often associated with a reactive diluent in the aim to reduce the solution viscosity [22]. Pure epoxy samples were prepared by mixing Tetra (80 wt%) with Bi resin. The fluorinated acid (4% of the total weight: TetraBi + F + Hardener) was slowly added at 80 ± 5 °C. The mixture was magnetically stirred until the obtention of a homogeneous brown compound.

2.2.1.3. Preparation of the uncured Tetra(BiF). The fluorinated bi-epoxy resin (BiF) was also synthesized before mixing with the tetra resin. A ratio of the epoxy to the acid carboxylic acid group of 0.5 was fixed. The mixture was magnetically stirred at a temperature of 72 ± 3 °C for 25 min.

The fluorinated Tetra(BiF) resin was obtained after mixing Tetra and BiF at 75 °C for 5 min. The quantity of the BiF added to the Tetra resin was adjusted to get a proportion of F of 4 wt%.

2.2.1.4. Preparation of the uncured Tetra for the fluorinated commercial-grade resin. The fluorinated resin was prepared by first mixing the perfluorononanoic acid (F) and the liquid tetra epoxy resin, at a temperature of 80 °C, for 15 min. The quantity of F used in the reaction was selected to obtain a final concentration of 4 wt% in the final fluorinated resin

2.2.2. Curing procedure

The curing of virgin or fluorinated epoxy mixtures was performed in commercial aluminum pans (Fisher Scientific, France). Pans were used without any surface preparation. After cooling the uncured fluorine-grafted tetra-resin, the hardener was introduced in stoichiometric quantity at 50 °C to get a lower viscosity. A constant volume of resin was introduced in each aluminum pan. A resin thickness of 1 mm was obtained after curing in a thermo-regulated oven.

The applied curing time was chosen from DSC experiments, in order to obtain a fully-cured resin. Curing kinetics of the epoxy resins were characterized with a Q-100 (TA instruments) differential scanning calorimeter (DSC) under both non-isothermal and isothermal conditions. Each measurement was performed with about 5 mg of epoxy resin, in an aluminum hermetic pan (TA instrument).

2.3. Sample surface analyses

The surface physicochemistry was investigated through contact angle measurements, using the sessile drop technique to determine the wettability of the surface. The surface energies were calculated using the Owens–Wendt method, developed in 1969 [24], which is based on the geometric mean equation and the static contact angles of reference liquids. Two reference liquids, typically a polar liquid (ultrapure water) and an unpolar liquid (diiodomethane), are necessary. Single drops (3 μL) of water and diiodomethane were placed on the surfaces of the samples, at room temperature. The contact angles (θ or CA) of the water (wCA) and diiodomethane (dCA) droplets were calculated based on the diameter, D, and the height, h, of the droplet on the surface, according to the following equation [25]:

$$\theta = 2\arctan\frac{2h}{D} \tag{1}$$

For each sample and each reference liquid, 10 measurements were performed at different positions of the resin surface. The free surface energy (γ_S) of the sample was then calculated from the Eqs. (2) and (3); the considered dispersive (γ_L^d) and polar (γ_L^p) components being 21.8 and 51.0 mJ m^2 respectively for ultrapure water, and 50.8 and 0 mJ/m^2 respectively for diiodomethane.

$$\gamma_L\cdot(1 + cos\theta) = 2\cdot\sqrt{\gamma_S^d\gamma_L^d} + 2\cdot\sqrt{\gamma_S^p\gamma_L^p} \tag{2}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{3}$$

FTIR spectra in MIR wavenumber range (4000–600 cm^{-1}) were recorded by using a Bruker VERTEX70 V. An attenuated total reflection mode (ATR) was chosen since the KBr substrate has been suspected to exhibit a catalytic activity on the curing reactions implying the tetra-functional epoxy [20]. The spectra were collected at a resolution of 4 cm^{-1} over 40 scans.

3. Results and discussion

3.1. Elaboration and curing of the fluorinated resin (TetraF)

Most of the commercial liquid resins used for the preparation of composite materials are multifunctionalized rather than di-epoxide molecules in order to obtain the best mechanical performances. One of

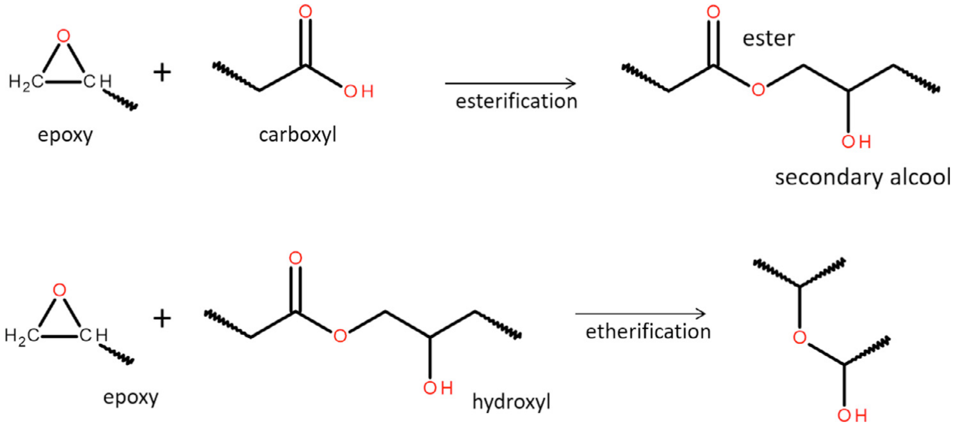

Fig. 1. Reactional pathway of the epoxide-carboxyl esterification and the epoxide-alcohol etherification.

these commercial resins was fluorinated in order to elaborate a non-adhesive modified epoxy resin [14] in the same manner as described for the DGEBA fluorination [12,13]. However, S. Rolere et al. [14] observed the dependence of its hydrophobic character on the number of curing steps and their temperature. A two-step curing procedure was recommended for reaching the highest level of surface fluorination.

In order to study the relationship between the surface properties of the cured material and the curing process, the Tetra resin was fluorinated and its curing was studied. The fluorination was carried out via an esterification corresponding to the addition of the carboxylic group of the perfluorononanoic acid on the tetra epoxide one. Such an esterification should not be completed, i.e. the addition of 4 perfluoro acid molecules onto 1 tetra molecule, because the steric hindrance of such a tetrafunctional molecule is not negligible [26]. However, in presence of the tertiary amino groups the reaction should be specific [27].Indeed, the carboxyl-epoxide reaction should compete with the hydroxyl-epoxide and carboxyl-hydroxyl reactions. However, in the absence of alcohol excess, the presence of tertiary amino groups should promote the carboxyl-epoxide reaction even if the etherification reaction could occur when the acid was completely reacted (Fig. 1). This reaction usually takes place with a reasonable rate above 200 °C, and can consequently be neglected at the used temperature of 80 °C.

The evidence of the fluorination was given by the solution coloration alteration from blue just after the addition to brown after 15 min at 80 °C. The fluorination, followed by ATR-FTIR spectroscopy (not shown here), was characterized by a slight decrease of the intensity of the epoxide vibration band at 907 cm^{-1} [27–31] and the appearance of the carbonyl vibration band of the ester group at 1781 cm^{-1} [32].The relative epoxy contents for both tetra and tetraF resin were calculated as the ratio of the area under the peak at 906 cm^{-1} to the area under the peak corresponding to the aromatic C=C stretching band centered at 1614 cm^{-1}. From the ratio of these two values, we obtained a calculated reaction conversion of 4 wt% in agreement with the theoretical value of 1.5%. Moreover, this uncured fluorinated resin did not age since its ATR-FTIR signature (not shown here) remained constant for at least 12 days. Furthermore, the broad hydroxyl group's band centered around 3450 cm^{-1} presents for the pure tetra resin did not vary. Consequently, the hydroxyl functions, known to play a catalytic role in the epoxy-amine reactions, was considered as stable.

The homopolymerization of the tetra resin was investigated since, as with many multifunctional epoxy, the tetra resin could homopolymerize by cyclisation at quite low temperature that may compete with the crosslinking with the hardener [29,30]. The DSC curve (Fig. 2) of the tetra resin was in agreement with previously published results with a sharp peak starting around 292 °C and presenting a maximum at 317 °C [29]. Homopolymerization of the fluorinated resin was observed at a lower temperature (278 °C against 292 °C) and the reaction was less exothermal (806 J g^{-1} against around 1100 J g^{-1}). For the tetra resin, it was shown that the homopolymerization can be effective at a temperature of 150 °C providing a cured material with a Tg in the quite large range of 184 °C, as described in [33] after one week in air in absence of catalyst or curing agent [29]. Consequently, for the TetraF resin, the homopolymerization could compete with the other process at even lower temperatures than 150 °C.

Because of the viscosity of the liquid multifunctional resin, the curing agent addition usually takes place at higher temperature than the ambient one; it is generally comprised between 65 and 120 °C depending on the chemical structures of the two components (epoxy resin and hardener) [17,21,34–36]. Even if increasing the mixing temperature induced a better homogenization, the uncured TetraF and hardener mixing should be prepared close to the ambient temperature since the gelation starts at around 60 °C (cf Fig. 3). Besides, compared to the curing of the commercial resin described in [14], the faster gelation kinetic of TetraF should be unfavorable to the diffusion of the fluorinated species towards the surface (Fig. 3). As a consequence, the proportion of crosslinked TetraF molecules in the bulk could rapidly increase. DSC is an indirect method to monitor the curing reaction and a 100% reaction extent means that any further heat evolution was observed even if active groups can still exist.

The influence of the first curing temperature on the free surface energy of the crosslinked material was studied as suggested in [14] (Fig. 4).

As expected, the lowest free surface energy (25 mJ m^{-2}) was obtained at the lowest temperature (70 °C) at the resin/air interface with only one curing step. This experiment confirmed the competition between the resin curing and the diffusion of the fluorinated molecules. Increasing the temperature induces two effects: to decrease the solution viscosity that enhances the fluorinated groups diffusion but also to expand the tridimensional network formation [13,14]. In Table 1, the surface energy of TetraF resins are given after two different curing processes: (a) a two-step curing procedure with a first relatively high temperature step at 120 °C, followed by a thermal treatment at 180 °C, or (b) a four-step curing procedure composed of two additional pretreatments at lower temperatures (1 h at 60 °C and 1 h at 80 °C) which are supposed to enhance the diffusion of the fluorinated compounds. In addition, we assessed the effect of a 12 h post-curing at 120 °C.

As suggested in [14], the free surface energy of the cured TetraF resin was lowered from 31 mJ m^{-2} to 25 mJ m^{-2} when applying relatively low curing temperatures (60–80 °C) at the beginning of the curing procedure. Those values were very closed to the referenced one ($\gamma < 20$ mJ m^{-2}; Fig. 4). The free surface energy variation induced by the first step could be explained by the diffusion of the fluorinated species. A band centered on 906 cm^{-1} was still observed after the curing at 120 °C indicating that oxirane groups were present at the surface (not shown here). It can be explained by the fact that the secondary amine was far less reactive than the primary amine due to the

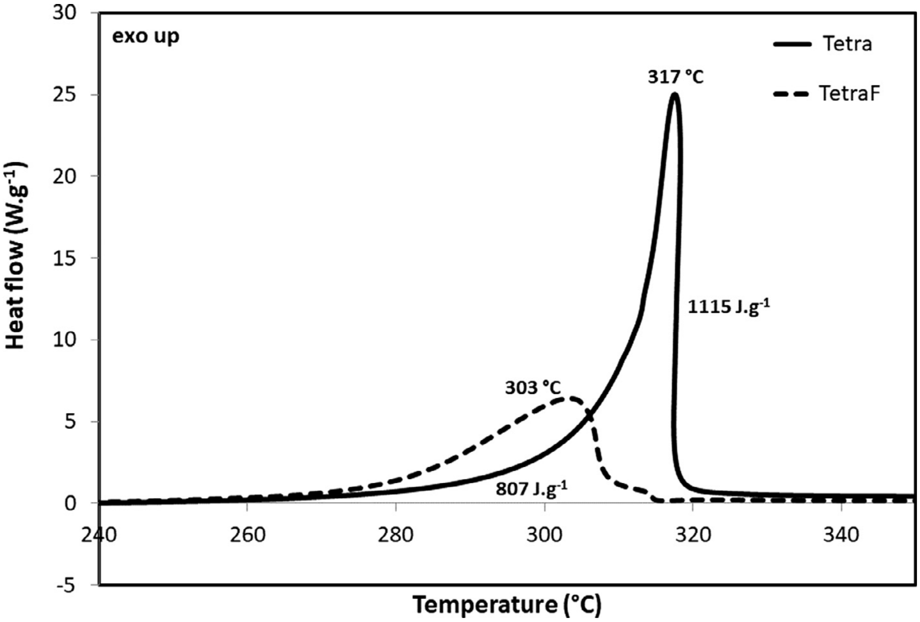

Fig. 2. DSC thermograms of the virgin (Tetra) and the fluorinated (TetraF) epoxy resins (rate = 10 °C min^{-1}).

steric hindrance. Indeed, from the NIR measurement on Tetra/4,4′-diaminodiphenyl sulfone (DDS), it was shown that 34% of the produced secondary amine were still present after 4 h at 160 °C [37]. At a temperature above 150 °C, the homopolymerization could occur generating alcohols and carbonyl groups, as proposed by Levchik [29], leading to the decrease of the band at 906 cm^{-1} and the increase of the bands at 1656 cm^{-1}. The latter could also be explained by the presence of amide group resulting from the oxidation of the surface. In addition, the OH band centered on ~3400 cm^{-1} was shifted to ~3300 cm^{-1} after the additional heating at 180 °C. Mailhot et al. [38], studying the photo and thermal degradation of a DGEBA/Jeffamine®D2000, explained this shift by the presence of hydrogen-bonded hydroperoxides and phenol end-groups. Consequently, the presence of these groups at the extreme surface could significantly increase the surface energy. However, our results indicated that with the four-step process, enough fluorinated compounds succeed in migrating to the surface during the two low temperature plateaux, screening the presence of these polar groups. The long post-curing at 120 °C appeared to also have an influence on the free surface energy, with a decrease to 22–23 mJ m^{-2}. This behavior was less expected and remains under investigation.

3.2. Elaboration and curing of the fluorinated (TetraBi)F resin

The epoxy composites as developed in aeronautic or automotive domains are generally composed of multifunctional epoxy molecules for the enhancement of the final mechanical properties. However, their high viscosity makes their manipulation much more difficult, especially in the case of spraying processes. Therefore, in most cases, some reactive diluent agents are added to assist the process. These agents also intervene in the obtained network if the added component is an epoxy molecule, such as the 2,2′-(butane-1,4-diylbis(oxymethylene))dioxirane (our “Bi” epoxy molecule). The Bi was mixed to the Tetra solution in the

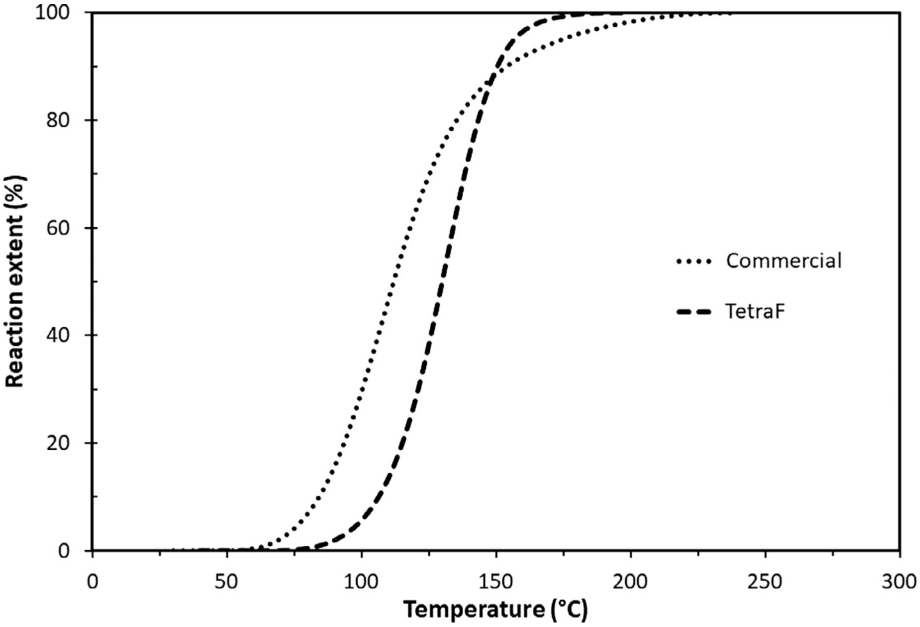

Fig. 3. DSC comparison of the commercial resin and the TetraF curing, mixed with the hardener in stoichiometric conditions (rate = 10 °C min^{-1}).

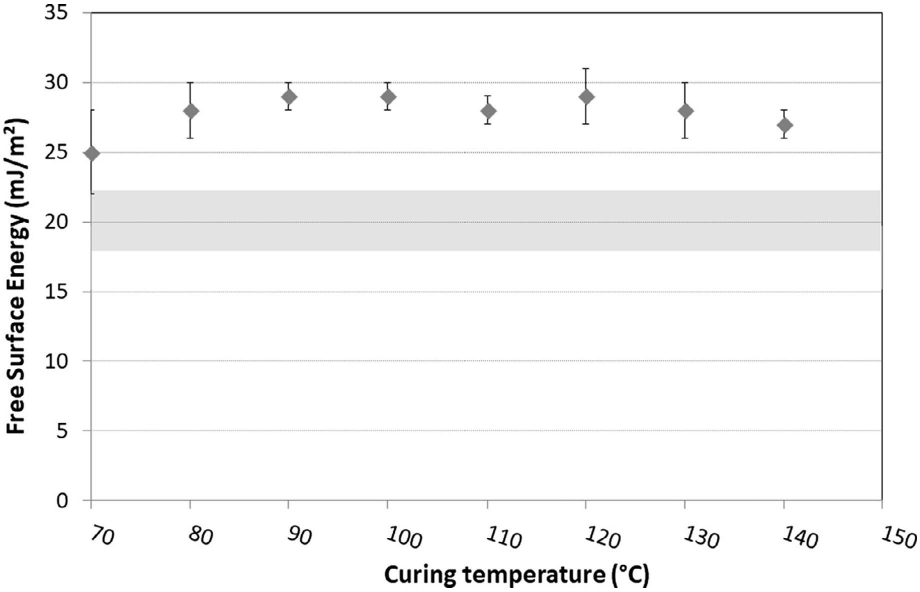

Fig. 4. Dependence of the free surface energy of the TetraF resin on the first curing step temperature (duration = 1 h, grey area: domain of referenced free surface energy).

Table 1
Dependence of the free surface energy of the TetraF on the curing process.

Curing (duration and temperature)	Post-curing (12 h − 120 °C)	Surface energy (γ, mJ m^{-2})
(1) 4 h at 120 °C + (2) 4 h at 180 °C	No	31 ± 2
	Yes	23 ± 4
(1) 1 h at 60 °C + (2) 1 h at 80 °C + (3) 2 h at 120 °C + (4) 4 h at 180 °C	No	25 ± 2
	Yes	22 ± 3

proportion of 20/80 wt% and the TetraBi was then fluorinated with 4 wt% of perfluorononanoic acid. The (TetraBi)F mixture was then crosslinked in presence of the hardener.

First of all, the crosslinking behavior of the (TetraBi)F mixture was analyzed by DSC analysis (Fig. 5). The comparison with the curing kinetics of the fluorinated commercial resin led to the conclusion that both resins have similar thermal behaviors [10], and could have very closed chemical formulation.

Then, the influence of the curing processes (number of plateaux, temperatures and durations) on the free surface energy of the cured material was also studied (Table 2).

As observed for TetraF, a first curing step at a low temperature (here: 15 h at 70 °C) led to the required free surface energy and gave the hydrophobic character to the material. Then, further curing steps either maintain or decrease this property. Indeed, the second step at 120 °C do not modify the surface energy (23 mJ m^{-2}) while the last step at 180 °C led to a quite strong loss of hydrophobicity. Such phenomenon during this last curing step could be explained either by the surface oxidation or the appearance of polar groups during the homopolymerization, the hydrophilic molecules (such as impurities) diffusion or the surface

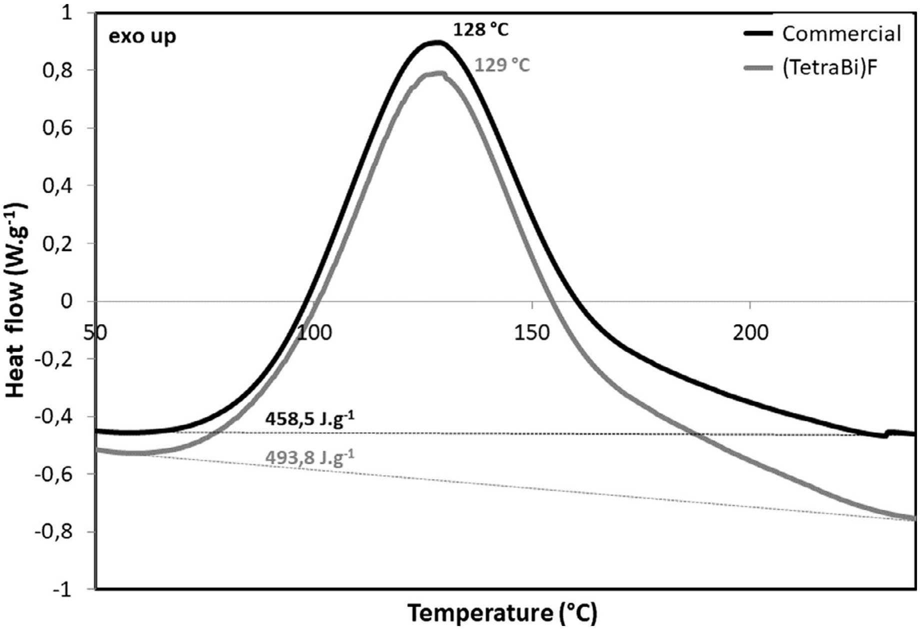

Fig. 5. DSC thermograms of the curing of the fluorinated commercial and (TetraBi)F resins, mixed with the hardener in stoichiometric conditions (rate = 10 °C min^{-1}).

Table 2
Dependence of the free surface energy of the cured (TetraBi)F resin on the curing process.

Curing (duration and temperature)	γ_s (mJ m^{-2})
(1) 15 h at 70 °C	23 ± 1
(2) = (1) + 2 h at 120 °C	23 ± 1
(3) = (2) + 2 h at 180 °C	36 ± 1

reorganization for minimizing the interfacial energy between the opposite interfaces, one being polar (air) while the other being apolar (fluorinated material). The surface oxidation was effective with the presence of the characteristic bands around 1750 cm^{-1} visible on the FTIR spectrum of the sample cured above 120 °C. However, it is probably not the main cause of the increase of the free surface energy, because such an increase was also observed when the curing was processed under a reduced pressure. Since the hydrophobic character of the cured TetraF was preserved whatever the curing parameters (Table 1), especially with along post-curing step, the Bi component might be involved in the increase of the free surface energy. In order to investigate this phenomenon, the curing of a Tetra(BiF) resin was then studied.

3.3. Elaboration and curing of the Tetra(BiF) resin

The bifunctional "Bi" resin was fluorinated with the same experimental procedure, i.e. in bulk. Such a fluorination led to the color alteration of the solution from blue to incolor. Although a ratio of epoxy to carboxylic acid groups of 0.5 was fixed, the band centered around 910 cm^{-1} completely disappeared suggesting that the oxirane groups had fully reacted. The C═O stretching band of perfluorononanoic acid crystal was initially centered approximately at 1751 cm^{-1} (monomer) and 1680 cm^{-1} (dimer). After the reaction, a relatively sharp band of medium intensity was present at 1780 cm^{-1}, as observed after the fluorination of DGEBA by the fluorinated acid [39], and assigned to the presence of the ester group. However, a small intensity shoulder can also be guessed around 1730 cm^{-1}. The intensity of this band increased when ageing our resins at 100 °C from 15 to 240 min. A similar behavior was observed after 27 days of storage at ambient temperature but with a less distinguishable shoulder. It is well known that these bands are assigned to C═O stretching group [29] but further investigations are required to conclude. Nevertheless, comparing these bands with those observed in the case of a pure fluorinated acid, we can think that the primary acrylation between the fluorinated acid and the oxirane groups was completed. The DSC analysis confirmed the instability of the BiF resin by showing after two days of storage, another exothermal peak starting 10 °C lower than for the fresh solution (75 °C). Hence, BiF was mixed to Tetra resin immediately after the fluorine addition. The FTIR signature over 12 days remained almost constant for Tetra(BiF).

As observed in Fig. 6, the thermal behavior of Tetra(BiF) was comprised between the one of the pure Tetra resin and the one of the fluorinated counterpart (TetraF).

The curing agent was then added in equivalent proportions to the TetraF and the Tetra(BiF) resins and the curing kinetics was followed by DSC measurements (Fig. 7). With the Tetra resin, the crosslinking reaction was initiated at higher temperature. It is important to note that in the case of the Tetra(BiF) resin, the crosslinking seemed to begin at a temperature close to the one applied to reduce the viscosity during mixing the resin with the hardener, i.e. 50 °C. Moreover, the Tetra(BiF) kinetics was faster than that of the commercial grade and close to that of the TetraF resin (see Fig. 8).

The influence of the temperature of the first curing step on the free surface energy of the cured Tetra(BiF) resin was studied (Fig. 7). As observed with the TetraF resin (Fig. 4), the lowest surface energy (≈ 21 mJ m^{-2}) was reached when the first-step temperature was below 100 °C. Higher curing temperatures led to an increase of the free surface energy with final values approximately equal to 33 mJ m^{-2}, when cured at temperatures higher than 150 °C.

At the end, with a complete curing process, several conclusions may be drawn (Table 3). First of all, an initial curing at a low temperature is requested to obtain the lowest hydrophobic character on the cured Tetra(BiF) resin (21 mJ m^{-2} at 70 °C). The overall thermal cycle induced a little increase of about 3 mJ m^{-2}and the further post-curing step had surprisingly no significant effect when compared to the results with (TetraBi)F.

3.4. Discussion on the surface behavior of the different cured fluorinated resins

The optimal curing cycles, leading to the highest hydrophobicity for each fluorinated resin, were summarized in Table 4.

With the aim to be applied to an industrial process for aeronautic

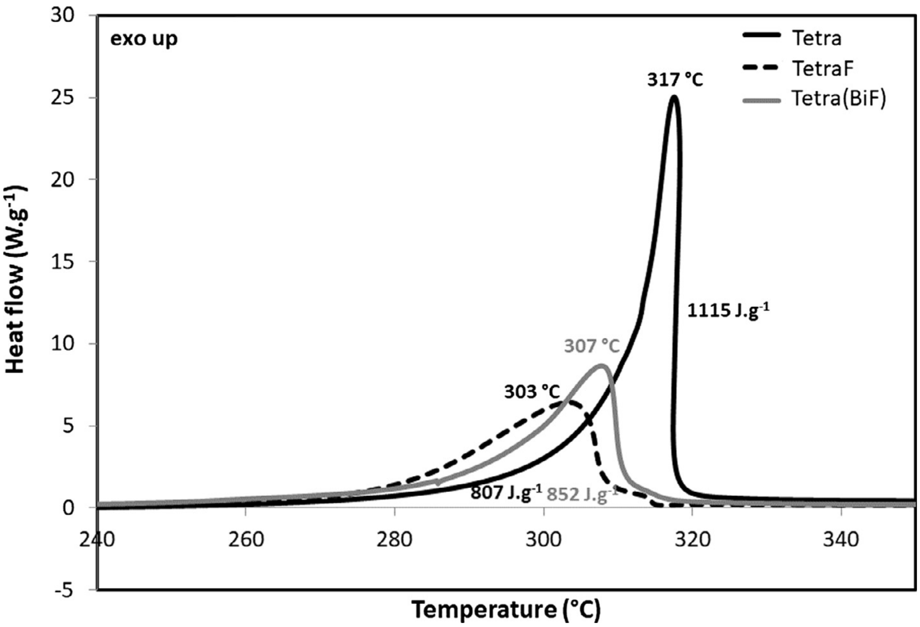

Fig. 6. Comparison of the thermal behavior of the Tetra(BiF), the Tetra and the TetraF resins (DSC thermograms, rate = 10 °C min^{-1}).

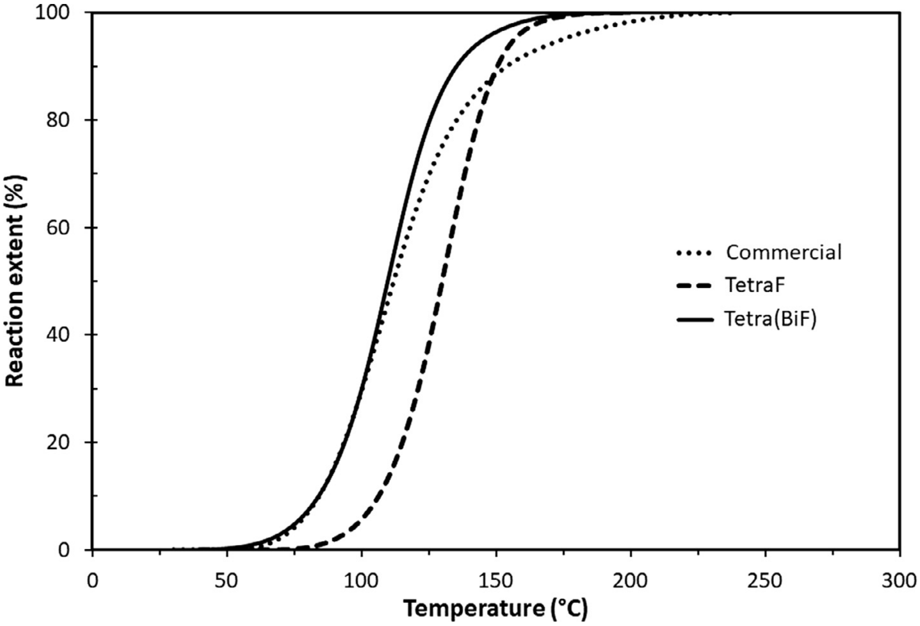

Fig. 7. DSC thermograms and curing kinetics of the commercial grade, the TetraF and the Tetra(BiF) resins mixed in stoichiometric conditions with the hardener (rate = 10 °C min^{-1}).

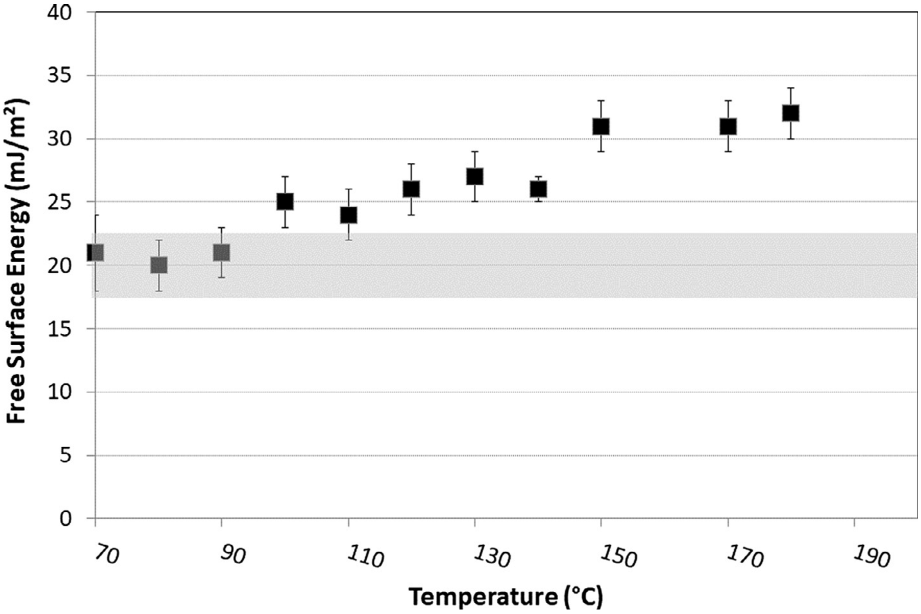

Fig. 8. Influence of the temperature of the first curing step on the free surface energy of the Tetra(BiF) resin (80/20 wt%) (duration = 1 h, grey area: domain of referenced free surface energy).

Table 3
Dependence of the free surface energy of the Tetra(BiF) resin on the curing process.

Curing (duration and temperature)	γ_s (mJ m^{-2})
1 h at 70 °C	21 ± 2
(1) = 1 h at 60 °C + 1 h at 80 °C + 2 h at 120 °C + 4 h at 180 °C	24 ± 2
(2) = (1) + 12 h at 120 °C	24 ± 4

applications, the TetraF and the Tetra(BiF) resins had a free surface energy not so far from the target values (18–20 mJ m^{-2}). For a temperature above 150 °C, the homopolymerization of the tetra-functional epoxy resin led to the presence of polar groups at the surface of the samples. These groups were probably screened by the presence of the fluorinated compounds depending on their coefficient of diffusion. In the case of the Tetra(BiF) resin, the fluorinated compounds were low molecular weight molecules. So, we can suppose that the two first steps at low temperature were sufficient to allow the saturation of the surface with these fluorinated compounds. On the contrary, with the (TetraBi)F and the fluorinated commercial resins, the reaction of acrylation can occur both on bi and tetra functional epoxy resins, leading to high weight fluorinated compounds with a low diffusion coefficient. However, a long post-curing treatment at 120 °C, as done for the TetraF resin, could reduce the surface energy. Nevertheless, a more complete investigation is required to understand this phenomenon. On the other hand, the fluorination mechanism and kinetics have to be well known and controlled, especially when the studied materials are of industrial grade and often composed of multifunctional epoxy molecules.

Table 4
The lowest free surface energy of the different fluorinated resins.

Resin	Curing cycle(duration and temperature)	γs (mJ m-^{2})
TetraF	1 h at 60 °C + 1 h at 80 °C + 2 h at 120 °C + 4 h at 180 °C + 12 h at 120 °C	22 ± 3
Tetra(BiF)	1 h at 60 °C + 1 h at 80 °C + 2 h at 120 °C + 4 h at 180 °C	24 ± 2
(TetraBi)F	15 h at 70 °C + 2 h at 120 °C + 2 h at 180 °C	35 ± 1
Fluorinated commercial resin	2 h at 40 °C + 1 h at 60 °C + 1 h at 80 °C + 2 h at 120 °C + 4 h at 180 °C	32 ± 2

4. Conclusion

The free surface energy of a commercial fluorinated epoxy resin was shown to be dependent on the curing temperature: the higher the curing temperature, the higher the surface energy. This increase is neither dependent on the additives, or on the thermal surface oxidation. In order to understand the surface energy degradation, different fluorinated model resins were prepared and cured with various thermal cycles.

First of all, a tetra-functional resin, the tetraglycidylmethylenedianiline (TGDDM) was fluorinated with a perfluorononanoic acid then cured in presence of 4′-methylenebis (2,6-diethylaniline) as the curing agent. A multi-step curing procedure allowed maintaining the hydrophobic character induced by the fluorine grafting on the liquid resin. The first curing-steps at low temperatures (100 °C) and a post-curing at a higher temperature (120 °C) were found to be needed to reach the best surface hydrophobic character. Then, different formulations of this tetrafunctional epoxy resin with a bifunctional epoxy molecule (2,2′-(butane-1,4-diylbis(oxymethylene))dioxirane) as a reactive diluent agent, were fluorinated and cured. When the mixture was directly fluorinated in a one-pot procedure, the hydrophobic character induced by the first curing step (at a low temperature) was partially lost and reached a similar value than the one obtained with a commercial-grade resin. On the contrary, when the bifunctional component was previously fluorinated before being added to the tetrafunctional resin, the corresponding cured material preserved its hydrophobicity after a complete curing cycle (first step at a low temperature and a post-curing at high temperature). Consequently, this study demonstrates the influence of the fluorination mechanism and so, the need of controlling such reactions in complex formulations.

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