



# Surface migration of fluorinated additive during the curing of epoxy resin



P. Glaris<sup>a,b,c</sup>, J.F. Coulon<sup>b</sup>, M. Dorget<sup>a</sup>, F. 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 n° 6283, Institut des Molécules et Matériaux du Mans – département Polymères, Colloïdes et Interfaces, Avenue Olivier Messiaen, 72085 Le Mans Cedex, France

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## ABSTRACT

Driving forces, responsible for the migration of a fluorinated additive added to a thermoset resin, toward the air/solid interface, were investigated. On this subject, the surface chemistry as characterized by XPS analyses was compared to theoretical models based on the rheological properties of the blend. It appears that the migration of the fluorinated molecules toward the surface cannot be described by a conventional diffusion model. A second model derived from the latter suits better to the experimental data and should be presented as another proof that additional motion forces drive the fluorine molecules migration in curing epoxy resin.

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## 1. Introduction

Fluorinated molecules as additives are well suitable for the preparation of low surface energy materials and numerous papers deal with the decrease of surface energy of polymers thanks to the incorporation of such molecules [1–8]. This behaviour was related to the migration of the fluorinated chains at the air/solid interface thus, leading to the surface enrichment in fluorinated groups, well known for their low surface energy [9,10]. For blends composed of thermoplastic polymers, evidences of such a migration phenomena were given [4,11–16]. This migration was explained by the presence of a thermodynamic driving force [4] not only resulting from the gradient of the surface energies between the fluorinated part and the host polymer [11,12] but also from the difference between the molecular weights of fluorinated molecules and the host polymer [13–16]. It should be pointed out that no evidence was given on these driving forces responsible for the migration in a thermosetting host polymer, even if the concept was applied to thermoplastic blend [6,7]. Moreover, for such a blend, the transition between the oligomeric and polymeric states must be taken into account. Indeed, in the oligomeric state, each molecule can independently move inducing high blending entropy and a good misci-

bility of the components even those with low affinities. In an opposite manner, at the gel point corresponding to the macromolecular lattice appearance, the chain motion is reduced leading to a decrease of the blend entropy and miscibility. The phase segregation observed during the curing of the thermoset polymer in presence of thermoplastic modifiers was also explained by this transition [17,18]. In this work, we investigated how a fluorinated additive migrates to the surface of a modified epoxy resin during its curing. To this purpose, a theoretical relationship between the curing temperature of the resin and the final surface composition was first set up and then, compared to the experimental data extracted from contact angle and XPS measurements.

## 2. Experimental part

### 2.1. Products

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin Poly-pox E064 (purity 100%) was supplied by Dow Chemicals (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: perfluorodecanoic acid (F13), perfluorononanoic acid (F17) and perfluorododecanoic acid (F23) were supplied by Aldrich (France). All products were used as received.

\* Corresponding author. Tel.: +33 (0)243832698; fax: +33 (0)243833558.

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

## 2.2. Substrate synthesis

Fluorinated epoxy resins were synthesized by first mixing the perfluorinated acid and the DGEBA leading to the formation of an ester [6,19] as described in the schematic reaction pathway (Fig. 1). The complete reaction of fluorinated acids to the epoxy resin is proven by the shift of the carbonyl FTIR absorption band from  $1771\text{ cm}^{-1}$  (characteristic of a carboxylic acid function) to  $1781\text{ cm}^{-1}$  (characteristic of an ester group) [20]. Then, a stoichiometric amount of curing agent (MDEA) relatively to that of DGEBA is added and the whole blend is cured at a given temperature during the time needed to reach the gel point (Fig. 1). Whatever the additive, its concentration was kept constant and equal to 1 wt% of the final blend. The curing of samples for surface analysis was performed in an aluminium cup of 50 mm diameter in a standard oven at atmospheric pressure. A controlled quantity of blend was poured in the cup in order to produce 1 mm thick samples.

## 2.3. Rheological properties of the blend

Rheological studies of the blends were realized with an ARES G2 rheometer which allows an imposed strain (TA Instruments). A

planar geometry was used for all the measurements thanks to two flat plates of 25 mm or 40 mm diameter. Plates of 25 mm diameter were used for the monitoring of rheological behaviour of the blend at given temperatures whereas 40 mm diameter plates were used for the viscosity measurement since the bigger torque induced by these plates leads to more reliable measurements of low viscosities. The blend mixture was placed on the lower plate once the plate's temperature reaches the fixed one. An average threshold of  $1 \pm 0.1\text{ mm}$  was imposed between the upper and lower plates in order to keep the same blend volume for each measurement. An initial 200% stress was set up to reach easily the imposed strain when the viscosity is still low. This stress is automatically decreased during the test when the strain value is overloaded.

## 2.4. Surface properties

Before to be analysed, the surface sample, which was in contact with air during the curing of the blend, was washed with acetone which is a good solvent of the fluorinated additives in order to prevent that any not grafted fluorinated molecules remain at the sample surface.

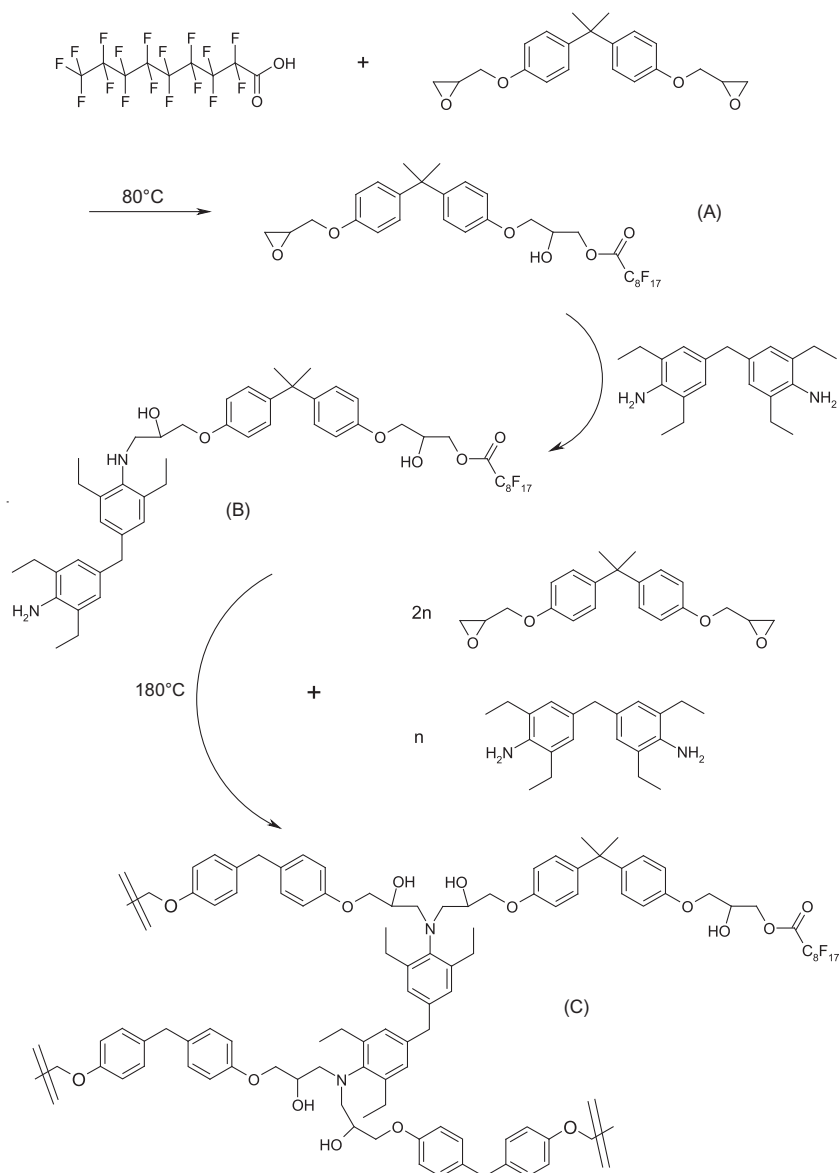


Fig. 1. Reaction pathway of fluoroalkanoic acid addition and DGEBA curing.

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