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Fluorinated epoxy resin as a low adhesive mould for composite material

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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.

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 Polypox E064 (purity 100%) was supplied by Dow Chemicals

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

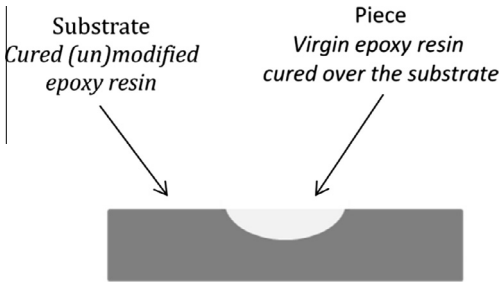

Fig. 1. Schema of substrate bearing a hemispherical cavity poured with liquid epoxy resin afterward cured.

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 (≈2 wt%) than for epoxy resins modified with F17 (≈3 wt%) and F13 (≈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 (γ_S) obtained for each additive was determined (Table 1). As expected, γ_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