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Experimental evidence of the interface/interphase formation between powder coating and composite material

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ABSTRACT

The present study focuses on the physicochemical characterization of the interface between an epoxy/polyester-based powder coating and an epoxy/thermoplastic-based composite material. An in-mold process has been used for the powder coating deposition on carbon/glass fibers reinforced composite substrates, and different methods have been performed to characterize the interface. We evidence here the strong dependence of the structural, chemical and thermal behaviors of the interface on the cure time/temperature conditions at which the powder coating was crosslinked. At a low crosslinking rate of coating (~48%), experimental results reveal the development of a large heterogeneous organic/organic interphase between coating and substrate. However, thin interphases have been detected when the crosslinking rate goes beyond 69%. Besides, a phase segregation of thermoplastic additive within the composite matrix was identified in the formation of this interphase. Energy-dispersive X-ray spectroscopy (EDS) as well as FTIR/Raman experiments enabled us to put in evidence the diffusion process of the thermoplastic additive toward the coating. From thermal analysis, glass transition temperature *Tg* for both components was observed, which confirm the proposed mechanism. This study highlights the importance of the thermal processes on the complex competition between the interdiffusion between two epoxy matrix and the existence of thermoplastic toughening agent at the interface of powder coating and composite material.

1. Introduction

In automotive and aeronautic applications, substrates are coated for protective, functional and/or decorative purposes. Such applications are strongly impacted by the recent regulatory constraints REACH (Registration, Evaluation, Authorization & restriction of Chemicals) which aim to eliminate hazardous products, and to limit volatile organic compounds (VOCs). The manufacturers look for an environmentally way of painting like powder coating which is a completely solvent-free product [1–3]. Over the past years, the use of powder coatings has been increased due to their environmental attributes, economic benefits and performance advantages. The ability to apply this modern environmentally coating on metal and heat resistance materials are a real advantage for industrial applications [1,4,5].

Practically, the classical deposition method of the powder coatings is realized by flowing it to the substrate through a gun, which applies an electrostatic charge for the polymer particles. The coated substrate is then heated in a curing oven in order to coalesce the polymer particles and form a continuous film on surface. Here, the nature of the substrate plays a major role in adhesion mechanisms of powder coatings. When using a metal substrate, this procedure shows successful results due to the conductive properties of the metallic substrate and its good resistance against deformation at high temperature [6,7]. However, when the substrates are heat sensitive, electrical insulating and/or polymer based materials, some problems related to the adhesion strength and curing temperature can limit the application of the powder coatings. In this case, surface activation processes like flame spraying, corona and plasma treatments, or the use of electrical solvent-based conductive primer and adhesion promoters are strictly required [8–10]. The enhancement mechanisms that result from these treatments include (i) increasing the surface area and

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thus the total interfacial bonding energy; (ii) improving mechanical interlocks by surface roughening; and (iii) changing the nature of the surface states to those having higher polarity and thus stronger interactions [11].

It is well known that the adhesion between two materials is highly dependent on the characteristics of the interface that separates them. In this region, interphase formation occurs due to physical and chemical interactions, and its width depends on the interfacial interaction mechanisms as well as on the nature of the bonded materials [12–14]. Therefore, the variation in mechanical and chemical properties across the interphase plays a major role in the optimal performance of the interface and adhesion strength [15–17]. In the case of assembling high *Tg* thermoplastic with thermoset epoxy/amine networks, the structure and the thickness of the interphase are related to the chemical composition, the miscibility of the components. They also depend on the processing conditions of time and temperature and the diffusivity of the thermosetting monomers into the thermoplastic [18,19]. In composite and adhesive systems, the change in the epoxy/curing agent stoichiometry affect the structural and the thermomechanical properties of the network. As the amine curing agent tends to adsorb on the surface, the local microstructure and resulting properties that develop will likely be affected, thus creating an interphase region with properties different from the ones of the bulk resin [20]. In this way, the knowledge of the physicochemical properties of the interphase is essential when designing multi-component materials such as fiber-reinforced matrix and protective coatings [21–23].

In this study, our objective is to present an alternative method for the powder coating deposition on composite substrate, and obviously to characterize the organic/organic interphase generated between the epoxy/polyester-based powder coating and the epoxy/thermoplastic-based composite material. In order to understand the adhesion mechanisms, the influence of cure time/temperature conditions on the interphase characteristics has been investigated. Physical and chemical analyses have been performed to highlight in depth the properties of the adhesive interface. SEM microscopy and MTDSC analysis have been used to study the structural and thermal properties. EDS analysis and FTIR/Raman spectroscopies have been applied to chemically identify the different components of the interphase.

2. Experimental

2.1. Materials

The powder coating used in this work consists of epoxy/polyester (EP) resins. EP powders were essentially constituted by a mixture of diglycidyl ether of bisphenol A (DGEBA), polyester resins, mineral fillers and pigment. The diameter of the granulometric distribution ranges from 5 to 40 μm. The composite substrate is a modified epoxy/thermoplastic matrix prepreg with glass and carbon fibers. It has been produced by laying up pre-impregnated (prepregs) laminates followed by a curing treatment.

2.2. Sample and cross section preparation

In order to prepare the coated-composite substrates, an in-mold powder coating process has been performed (Fig. 1a). The principle of this process is different from that of the classical deposition method already defined in the introduction part of this work.

Firstly, release agent is applied on the mold. The EP powder coating was sprayed by electrostatic gun onto a conductive mold then heated at 120 °C for different times. At this stage, the powders flow

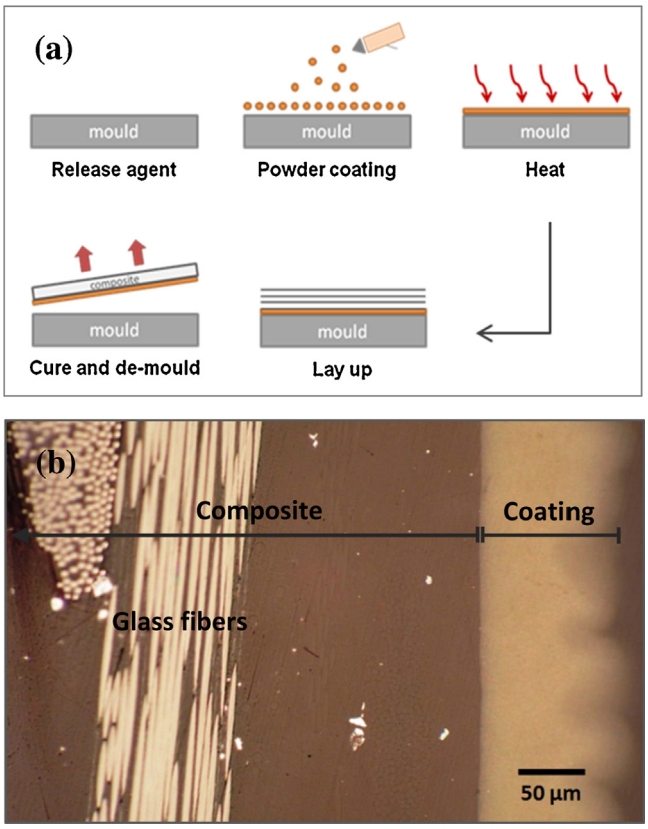

Fig. 1. (a) Schematic diagram illustrating the general process of in-mold powder coating and (b) optical image of a cross section sample showing the interface region between the coating and the composite substrate.

and coalesce to form partially crosslinked films. Next, the sheets of prepreg composite materials were laid up on pre-heated powder layer, and the in-mold coating composite samples were fully cured and chemically bonded with a curing cycle (2 h at 120 °C and 2 h at 180 °C) [24]. To study the effect of conversion rate of the powder coating on the interface properties, different samples were prepared by varying, in the first stage, the pre-heating time of the powder coating in the mold (20 min, 40 min, 60 min). The conversion rates of the pre-heated EP powder coating were calculated from DSC measurements, and reported in Table 1. For the SEM and FT-Raman analyses, the coated composite substrates were cut and embedded in acrylic resin. The samples were cross-sectionally polished with 400 and 1200 silicon carbide grinding papers using water as lubricant. Subsequently, they were polished with diamond pastes of 6 μm, 3 μm and 1 μm using alcohol based lubricant. The polishing velocity was about 300 rpm and the samples were cleaned with water and dried under air flow to eliminate the remnant debris of the polishing process.

2.3. Characterization techniques

2.3.1. Scanning electron microscopy (SEM)

Samples were analyzed using a scanning electron microscope (SEM) coupled with energy dispersive X-ray detector (Zeiss Supra

Table 1
Values of the conversion rates of epoxy/polyester powder coating as determined by DSC analysis.

Condition	Conversion rates (±5%)
20 min, 120 °C	48%
40 min, 120 °C	69%
60 min, 120 °C	92%