

The effect of manufacturing technologies on the flame retardancy of carbon fibre reinforced epoxy resin composites

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Introduction

Carbon fibre is considered as benchmark fibre reinforcement in many structural polymer composite applications. In order to propose a tailored fire retardancy solution for these composites, it is necessary to clarify the possible effects of carbon fibre reinforcement on the fire performance [1].

First of all, the high thermal conductivity of the carbon fibres facilitates the ignition of the composites, which phenomenon is addressed as the candlewick effect. In the case of flame retardants (FRs) acting in the solid phase, the carbon fibres not only interfere in their mode of action and hinder intumescent behaviour, leading to decreased fire performance, but on the other hand, the charring of the flame retarded matrix layers delaminates the layers of fibre reinforcement, leading to the loss of composite mechanical properties.

Furthermore, the applied FRs usually increase the viscosity of the polymer matrix, which is a key property during the production of composites by liquid transfer moulding techniques, such as resin transfer moulding (RTM). These productive technologies are increasingly used for the manufacturing of high-performance fibre-reinforced thermoset polymer composites, including structural automotive and aircraft components. In many of these applications, additives are required to improve some properties or to provide additional ones, such as flame retardancy. Many of these additives are solid-phase, thus the reinforcement layers may filter them during the RTM process, leading to non-uniform distribution and unpredictable performance [2].

In the present work we investigated the effect of carbon fibre reinforcement and composite manufacturing technologies on the fire performance of epoxy resins, with special emphasis on the particle distribution of solid flame retardants.

Experimental

As matrix materials we applied low-viscosity, potentially renewable trifunctional glycerol- (GER) and a tetrafunctional pentaerythritol-based (PER) epoxy resin (EP) cured with a cycloaliphatic amine-type hardener. As flame retardants we applied solid phase ammonium polyphosphate (APP), acting in the solid phase, liquid resorcinol bis(diphenyl phosphate) (RDP), acting predominantly in the gas phase, and their combination, which proved to be synergistic in terms of fire retardancy in previous studies of the authors [3]. A unidirectional carbon fibre (CF) fabric was used as reinforcement. EP samples of gradually increasing P content (1%, 2%, 3%, 4%, 5%) from APP or from RDP were prepared in addition to mixed formulations with 2% P content from APP and 2% P content from RDP. Composite laminates with 3% P content in the matrix were made both by hand lamination followed by hot pressing and by

RTM method. In order to model the suspected gradient of APP filtration in the case of RTM, a composite sample containing different amount of P (1%, 2%, 3%, 4%, 5% P) in each subsequent matrix layer was prepared by hand lamination followed by hot pressing.

Fire retardancy of matrix and carbon fibre reinforced specimens was evaluated by limiting oxygen index (LOI), UL-94 tests and mass loss calorimetry. The temperature dependence of the matrix viscosity was determined by parallel plate rheometry. The thermal stability of the matrices was investigated by thermogravimetric analysis, while the effect of FRs on the glass transition temperature and crosslinking process was studied by differential scanning calorimetry in matrices and by dynamic mechanical analysis in composites. The distribution of APP was studied by scanning electron microscopy with energy dispersion spectrometry (SEM-EDS) in the composite cross-section.

Results and discussion

According to the flame retardancy results, the inclusion of carbon fibres itself increased the limiting oxygen index (LOI) and peak heat release rate (pHRR), but most of the samples burned to the clamping during the vertical UL-94 test, probably due to the high thermal conductivity of the included carbon fibres. With the same FR content, PER delivers better fire performance than GER. In both systems the combined solid and gas phase FR action proved to be favourable. To the extent of our knowledge, for the first time SEM-EDS method was successfully used to prove the filtration of solid flame retardants in carbon fibre reinforced epoxy resin composites produced by RTM. Due to the accumulation of APP particles in the upper layers of the composite, the composite sample prepared by RTM had much lower pHRR and higher amount of residue than the one made by hand lamination followed by hot pressing. The fire performance of the RTM composite under mass loss calorimetry circumstances was closer to the performance of the model composite with the 5% P on the top, than the composite with the same overall P content prepared by hand lamination followed by hot pressing. Consequently, when applying liquid transfer moulding methods for the preparation of composites containing solid FRs, the filtration has to be taken into account. Another possible solution is to use a liquid flame retardant in the matrix, preferably acting mainly in the gas phase during combustion, and separate flame retardant coating or a multi-functional gelcoat with flame retardant properties.

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