

THE EFFECT OF RESORCINOL BIS(DIPHENYL PHOSPHATE) ON THE FLAMMABILITY AND FLEXIBILITY OF FLAME RETARDED EPOXY GELCOATS

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Abstract: *During liquid composite moulding technologies, solid flame retardant (FR) particles can be filtered by the reinforcing structure during the injection. This can be avoided by using liquid-only FRs (e.g. resorcinol bis(diphenyl phosphate), RDP) or applying FRs in a coating. Intumescent gelcoats offer excellent fire performance, but they often contain lots of fillers, making the gelcoat brittle and rigid, which leads to cracking and detaching. We prepared epoxy gelcoats containing ammonium polyphosphate (APP) and RDP to control the viscosity, hardness, and thus the flexibility of the gelcoats. We prepared samples with 10% overall P-content with different ratios of APP and RDP. Our goal was to determine which combinations resulted in a viscosity low enough for spraying without a diluent and proper fire performance. The most promising compositions were sprayed onto carbon fibre-reinforced epoxy composites, and their fire performance was investigated using mass loss type cone calorimetry (MLC).*

Keywords: flame retardancy; multifunctional gelcoat; carbon fibre reinforced composites; phosphorus-containing flame retardants

1. Introduction

Carbon fibre reinforced epoxy resin composites are mainly used in aircraft engineering as structural components to replace metal parts. The high flammability of epoxy resins implies the critical need to effectively flame retard them while maintaining their mechanical properties [1]. Previous halogen-containing systems are increasingly being replaced by halogen-free flame retardants such as phosphorus (P). In addition to providing adequate flame retardancy, these materials pose fewer environmental and health risks when used. Some composite manufacturing technologies, such as hand lamination or wet compression moulding, are not productive enough for the aerospace industry; the difficult reproducibility and time-consuming parts production make these methods not profitable. There are more productive manufacturing technologies, such as liquid composite moulding methods (RTM, VARTM). However, if these technologies are used to process resins containing solid FRs, the solid particles may become trapped in the reinforcing structure during injection and may be filtered [2,3]. Particle filtration can be avoided by not adding flame retardants to the matrix material of the composite or by using liquid-only flame retardants (such as resorcinol bis(diphenyl phosphate), RDP) and/or applying a flame retardant coating/gelcoat on the component's surface. Still, there may be other advantages: in an intumescent coating, foaming is not inhibited by the reinforcing structure, and the foaming itself does not cause delamination; the coating protects the component and does not significantly affect the mechanical properties [3]. Although excellent fire performance can be achieved with intumescent gelcoats, they often contain a high amount of fillers, making the gelcoat brittle and rigid. The flexibility of these flame retarded gelcoats is crucial during the application because if the gelcoat is damaged, it cannot fulfil its protective function.

In our previous research [4], we studied the possibilities of applying the FRs in a separate layer on carbon fibre reinforced composites, and we prepared gelcoats containing both APP (acting in the solid phase) and RDP (acting mainly in the gas phase) since we found that the combination of APP and RDP has synergistic effects on the fire performance. In this study, our goal was to determine the composition with a low-enough viscosity to be applied by spraying without a diluent and providing proper fire performance. We prepared gelcoat samples with 10% overall P-content in different ratios of APP and RDP and investigated the viscosity, the thermal behaviour and the fire performance of the gelcoat materials. The most promising compositions were applied on non-flame retarded (reference) and flame retarded, carbon fibre reinforced epoxy resin composites made by vacuum infusion. The fire performance of the coated composites was carried out by mass loss calorimetry tests (MLC).

2. Materials and methods

2.1 Materials

We used Sicomin SG715 BLANC epoxy gelcoat with Sicomin SD802 hardener as reference and basis for the FR gelcoat formulations. The gelcoat was supplied by Poly-Matrix Ltd, Budapest, Hungary.

As matrix resin system for the composites a tetrafunctional pentaerythritol-based epoxy resin (PER; IPOX MR3016; producer: IPOX Chemicals Ltd, Budapest, Hungary; main component: tetraglycidyl ether of pentaerythritol; viscosity at 25 °C: 0.9-1.2 Pas; density at 25 °C: 1.24 g/cm³; epoxy equivalent: 156-170 g/eq) with a cycloaliphatic amine hardener (IPOX MH 3122; producer: IPOX Chemicals Ltd, Budapest, Hungary; main component: 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane; viscosity at 25 °C: 80-120 mPas; density at 25 °C: 0.944 g/cm³; amine hydrogen equivalent: 60 g/eq). The composite samples were prepared with unidirectional carbon fibre reinforcement (PX35FBUD030 consisting of Panex 35 50 k rovings, areal weight: 300 g/m²; supplier: Zoltek Ltd, Nyergesújfalu, Hungary) in [0]_s layup in each sample.

We used two phosphorus-based flame retardants: solid ammonium polyphosphate (APP; trade name: NORD-MIN JLS APP; producer: Nordmann Rassmann, Hamburg, Germany; P content: 31-32%; average particle size: 15 µm) and liquid resorcinol bis(diphenyl phosphate) (RDP; trade name: Fyrolflex RDP; producer: ICL Industrial Products, Beer Sheva, Israel; P content: 10,7%).

2.2 Methods

To investigate the viscosity, thermal behaviour and fire performance of the gelcoats, we prepared **gelcoat matrix samples**. Components were mixed according to the stoichiometric ratio recommended by the distributor (100:27). In the case of FR gelcoats, the FR additives were mixed into the epoxy component, and then the hardener was added. The prepared mixtures were poured into a silicone mould and cured for 24 h at room temperature. However, the hardener component was not added to the mixture for the viscosity measurement to avoid curing in the device. The prepared samples were the following:

- SG715_REF
- SG715_5P_APP_5P_RDP
- SG715_6P_APP_4P_RDP
- SG715_7P_APP_3P_RDP
- SG715_8P_APP_2P_RDP
- SG715_9P_APP_1P_RDP
- SG715_10P_APP

Sample names were built according to the following scheme: GELCOAT BASE_P-CONTENT IN MASS %_APP_P-CONTENT IN MASS %_RDP (e.g. SG715_6P_APP_4P_RDP means that the gelcoat base was the SG715/SD802 system, which contained 6% phosphorus from APP and 4% P from RDP).

For the coating process, **composite sheets** were **made by vacuum infusion** using a flexible vacuum bag. The reinforcement layers were stacked in $[0]_5$ layup. To promote and help the mould filling and the proper wetting of the reinforcement layers, we heated the resin mixture for 10-15 minutes at 60 °C to decrease its viscosity. We cured the samples for at least 24 h at room temperature under a vacuum before demoulding.

The coated composite sheets were prepared using a **spraying** gun (nozzle diameter: 2 mm) operating with compressed air (compressed air pressure: 2 bar). We repeated the spraying process until the proper thickness (approx. 500 μm) was achieved. The gelcoat thickness was continuously measured with a wet film thickness gauge.

The temperature dependence of the **viscosity of the gelcoats** was investigated by parallel plate rheometry using a TA Instruments AR2000 device (New Castle, DE, USA). We used a temperature range of 25-80 °C with a temperature ramp of 5 °C/min and a shear rate of 0.1 s^{-1} .

The **thermal behaviour of the gelcoats** was investigated by differential scanning calorimetry (DSC; TA Instruments Q2000 device, New Castle, DE, USA) and thermogravimetric analysis (TGA; TA Instruments Q500 device, New Castle, DE, USA) both in a nitrogen atmosphere. The **DSC** measurements allowed us to determine the effect of the changing APP:RDP ratio on the glass transition temperature (T_g) and the crosslinking characteristics of the gelcoats. We used a heat/cool/heat cycle in each case: first heating from 25 °C to 250 °C with a heating rate of 3 °C/min; cooling from 250 °C to 0 °C with a cooling rate of 10 °C/min; second heating from 0 °C to 250 °C with a heating rate of 10 °C/min. The crosslinking characteristics were determined from the first heating, while T_g was determined from the second heating. The effect of the APP:RDP ratio on the thermal stability of the gelcoats was investigated by **TGA**. The samples were heated in a temperature range of 25-800 °C with a heating rate of 20 °C/min.

We investigated the effect of the APP:RDP ratio on the **fire performance** of the gelcoat by standard limiting oxygen index (LOI) test, UL-94 flammability test and mass loss type cone calorimetry (MLC). The size of the samples used for the LOI test was 120 x 15 x 4 mm. We determined the **LOI** according to ASTM D2863: the oxygen index is the lowest volume fraction of oxygen in an oxygen-nitrogen gas mixture at which the sample burns for more than 3 minutes or burns for a 50 mm section on the specimen during the test. **UL-94 tests** were according to ASTM D3801 and ASTM D635 standards to determine the fire performance of the gelcoats in horizontal and vertical test setups. The dimensions of the samples were 120 mm x 15 mm x 4

mm. The UL-94 classifications in increasing order are HB, V-2, V-1 and V-0. The **MLC tests** were performed using an instrument from FTT Inc. (East Grinstead, UK), according to ISO 13927. In the case of the gelcoats and the coated composites, a constant heat flux of 25 and 50 kW/m² was used, respectively. Gelcoat samples were 100 x 100 x 2 mm, while the coated composites were 100 x 100 x 2.5 mm in size. We used spark ignition during the test. The heat release rate and mass loss were continuously tracked along the burning process.

3. Results and discussion

3.1 Viscosity of the gelcoats

Although we determined the temperature dependence of the dynamic viscosity of the gelcoats, it is essential to mention that these materials are usually used at room temperature. Therefore, only the viscosity values at 25 °C are shown in Figure 1.

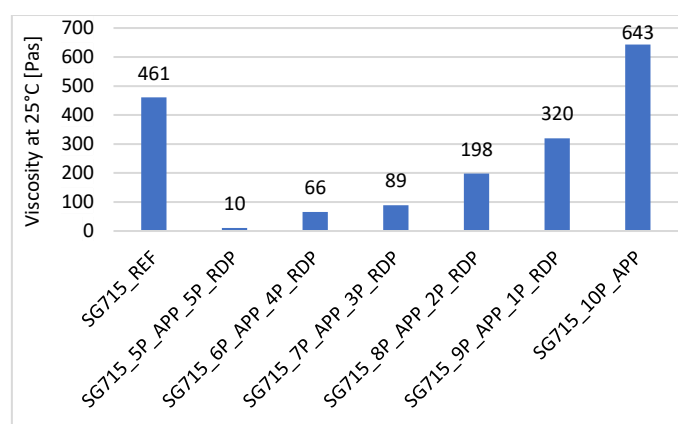


Figure 1. Dynamic viscosity of the gelcoats at 25 °C

The recommended application of SG715 gelcoat is brushing, as its viscosity is relatively high, and the solid APP dispersed in the resin further increases it, making the gelcoat unsuitable for spraying. However, the viscosity of the gelcoat can be adjusted by the addition of a diluting agent that evaporates during crosslinking, which makes spraying application possible. It is clear from the results that the dynamic viscosity of the gelcoats increases with the increasing APP ratio. On the other hand, the increasing ratio of RDP leads to a significant reduction of viscosity; therefore, the gelcoat becomes sprayable without diluent. In addition to viscosity reduction, RDP also eliminates the risk of forming solvent inclusions, as there is no need to dilute further the resin, which also results in a more compact gelcoat microstructure. Based on the results, we concluded that the gelcoats containing 6%P APP + 4%P RDP and 7%P APP + 3%P RDP could be suitable for spraying without diluting.

3.2 Thermal behaviour of the gelcoats

We performed DSC tests to determine the glass transition temperature and crosslinking enthalpy of the gelcoat samples. To better compare the results, we added the specific crosslinking enthalpy (h'_{spec}) to the list of results disregarding the amount of flame retardants since they reduce the crosslinkable material ratio of the resin (Table 1).

Table 1: DSC results of the gelcoats (T_{peak} : temperature of the exothermic peak; h' : reaction enthalpy; T_g : glass transition temperature)

Gelcoat	T_{peak} [°C]	h' [J/g]	h'_{spec} [J/g epoxy]	T_g [°C]
SG715_REF	75	188	188	97
SG715_5P_APP_5P_RDP	80	51	135	89
SG715_6P_APP_4P_RDP	77	64	147	97
SG715_7P_APP_3P_RDP	75	83	167	90
SG715_8P_APP_2P_RDP	73	102	183	107
SG715_9P_APP_1P_RDP	72	141	228	119
SG715_10P_APP	74	174	255	120

The addition of flame retardants did not affect the exothermic peak temperature, as it ranged 72–80 °C for all samples. The increasing ratio of APP led to increasing T_g . This can be explained by the well-dispersed spherical APP particles in the gelcoat [5] and the reduction in the RPD ratio. Due to the plasticising effect of RDP, it can decrease the T_g ; therefore, lowering the ratio of RDP leads to higher T_g . The addition of flame retardants resulted in lower crosslinking reaction enthalpy compared to the reference since the ratio of epoxy resin capable of crosslinking decreased.

We determined the temperature at 5% and 50% weight loss ($T_{-5\%}$; $T_{-50\%}$), the maximum mass loss rate (dTG_{max}) and its temperature (T_{dTGmax}) (Table 2).

Table 2: TGA results of the gelcoats

Gelcoat	$T_{-5\%}$ [°C]	$T_{-50\%}$ [°C]	dTG_{max} [%/°C]	T_{dTGmax} [°C]	Char yield at 800 °C [%]
SG715_REF	299	375	1.1	346	23.9
SG715_5P_APP_5P_RDP	233	345	0.7	301	31.8
SG715_6P_APP_4P_RDP	224	375	0.7	307	31.8
SG715_7P_APP_3P_RDP	229	388	0.7	310	36.8
SG715_8P_APP_2P_RDP	274	390	0.7	319	39.0
SG715_9P_APP_1P_RDP	243	399	0.6	309	39.1
SG715_10P_APP	300	475	0.9	329	43.2

The sample with 10%P APP started to decompose at the same temperature as the reference gelcoat; however, the samples containing both APP and RDP had 10-20% lower $T_{-5\%}$, indicating the different decomposition mechanisms of RDP and APP. The presence of RDP lowers the decomposition temperature, which is compensated by increasing APP content. The addition of flame retardants increased the $T_{-50\%}$ of all samples except the one with 5% P APP and 5% P RDP. The results clearly show that the applied FRs reduce decomposition rate, which can be an essential feature in a fire event, as the gelcoat burns more slowly, leaving more time for evacuation.

3.2 Fire performance of the gelcoats

We investigated the flammability properties of the gelcoat samples with limiting oxygen index and UL-94 tests. The results are summarised in Table 3.

Table 3: LOI and UL-94 classifications of the gelcoats

Gelcoat	LOI [V/V%]	UL-94 class.
SG715_REF	21	HB (23 mm/min)
SG715_5P_APP_5P_RDP	35	V-0
SG715_6P_APP_4P_RDP	40	V-0
SG715_7P_APP_3P_RDP	46	V-0
SG715_8P_APP_2P_RDP	50	V-0
SG715_9P_APP_1P_RDP	65	V-0
SG715_10P_APP	62	V-0

All FR samples achieved V-0 (self-extinguishing) classification in the UL-94 tests, which is promising, but not surprising given their 10% P-content. The limiting oxygen index results indicated that the optimal APP:RDP ratio is 9:1. The maximum LOI was reached by this composition, with a 30% increase from the gelcoat with an 8:2 FR ratio. The mixed FR formulations performed better than the gelcoat with 10% P APP, which can be explained by the combined solid and gas-phase effect of the flame retardants [5].

We analysed the fire performance of the gelcoat samples using mass loss calorimetry. Contrary to the composite samples, a heat flux of 25 kW/m² was used, as we expected high levels of foaming due to the high FR content. The heat release rates of the gelcoats are shown in Figure 2.

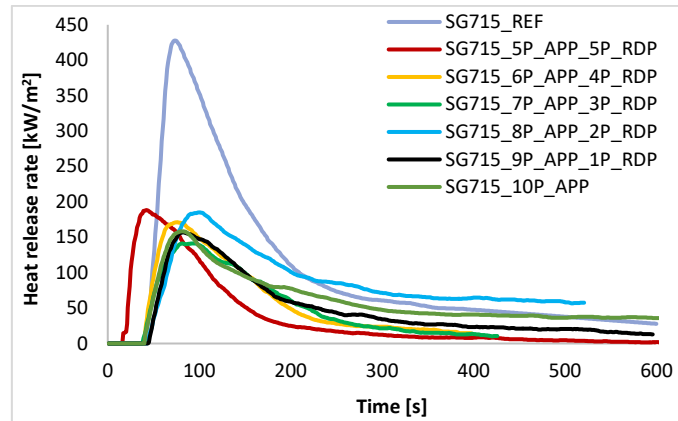


Figure 2. The heat release rate of the gelcoat matrices

During the experiment, the burning of the FR gelcoats was accompanied by intensive foaming and char forming. They also showed a significant reduction in the peak heat release rate and total heat release. While the reference sample had the highest pHRR (428 kW/m²), the flame-retarded gelcoats only reached the 150–200 kW/m² range. Interestingly, the gelcoat with 7% P APP + 3% P RDP reached the lowest pHRR (141 kW/m²), which is 67% lower compared to the reference. There is no significant difference between the TTI of the samples; the only exception is the sample with 5% P from both FRs, which ignited more than 20 s earlier than all other samples. The reduced TTI can be explained by the gas-phase mechanism of RDP. In addition, the increased amount of RDP significantly reduces the crosslinking density, which can also lead to lower decomposition temperature. Moreover, the FR gelcoats showed an increased time to pHRR and a more elongated, lower heat release. In terms of applicability and fire performance, the proper ratio of APP to RDP in the gelcoat matrix is either 6:4 or 7:3; therefore, in the next phase of our experimental work, we used these two gelcoat formulations to coat the composites.

3.3 Analysis of the coated composites

In the case of the coated composites, a heat flux of 50 kW/m² was used during MLC. The chosen composite samples (vacuum infused with 3% P RDP and a non-FR reference) were coated in 0.5 mm thickness with two different gelcoat matrices (6%P APP + 4%P RDP and 7%P APP + 3%P RDP) using a spray gun. The heat release rate of these coated composites is shown in Figure 3.

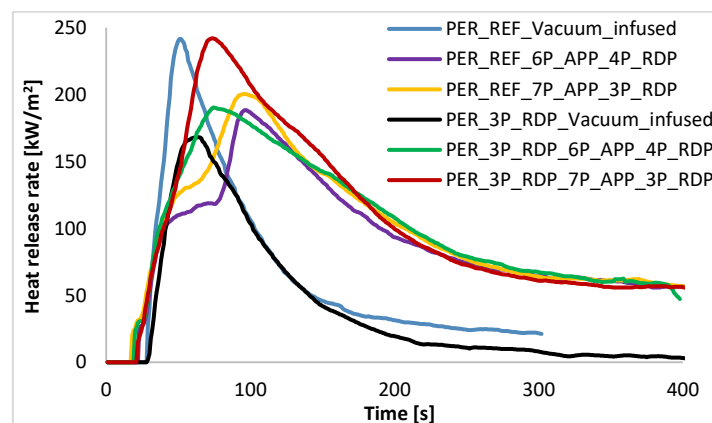


Figure 3. The heat release rate of the coated composites

The pHRR of the flame-retarded samples was in the range of 188–200 kW/m², and their THR was between 35 and 39 MJ/m². On average, the application of the FR gelcoats lowered the pHRR of the PER reference composite by 20%. As for the PER composite with 3% P RDP, the 6:4 gelcoat could lower the pHRR to the same extent as in the case of the coated reference, but the other gelcoat (7:3) reached as high pHRR as the PER reference composite without coating. In this case, the addition of a further flammable layer could not be compensated by the flame retardant content of the gelcoat. The lowest pHRR (188 kW/m²) among the FR coated samples was reached by the PER_REF_6P_APP_4P_RDP. It achieved a pHRR reduction of 22% compared to the uncoated PER reference composite and a 6% reduction compared to PER_REF_7P_APP_3P_RDP. The MLC results indicated that the gas-phase effect of 3% P RDP in the gelcoat was insufficient to reduce pHRR effectively; therefore, 6:4 is the preferred flame retardant ratio in the gelcoat formulation. Overall, the fire performance of both reference and FR composites was improved by applying FR gelcoats; however, the effect of the gelcoats was more significant in the case of the reference composite. These results show that it is not necessary to incorporate RDP in the composite matrix of the coated composites. The application of flame-retardants in the coating alone is sufficient to protect the composite.

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4. References

1. Toldy A, Szolnoki B, Marosi Gy. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polymer Degradation and Stability* 2011; 96:371-376
2. Louis BM, Maldonado J, Klunker F, Ermanni P. Measurement of Nanoparticle Distribution in Composite Laminates Produced by Resin Transfer Molding. ECCM16 – 16th European Conference on Composite Materials, Seville, Spain 22-26 June 2014
3. Pomázi Á, Toldy A. Particle distribution of solid flame retardants in infusion moulded composites. *Polymers* 2017; 9:250
4. Pomázi Á, Toldy A. Development of fire retardant epoxy-based gelcoats for carbon fibre reinforced epoxy resin composites. *Progress in Organic Coatings* 2021; 151:106015
5. Pomázi Á, Toldy A, Szolnoki B. Flame retardancy of low-viscosity epoxy resins and their carbon fibre reinforced composites via a combined solid and gas phase mechanism. *Polymers* 2018; 10:1081