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The Influence of Reinforcing Layers and Varnish Coatings on the Smoke Properties of Laminates Based on Selected Vinyl Ester and Polyester Resins

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Abstract. The smoke properties of non-flammable polyester-glass laminates with reinforcing layers and laminates with paint coatings in relation to base laminates, unmodified, were compared. The obtained parameters were referred to the requirements applicable in rolling stock. These results were compared with the results of smoke tests for polycarbonate, which as a construction and lining material does not meet the requirements of the EN 45545-2 European rolling stock [1].

Introduction

The wide use of polyester-glass laminates in rail transport results from their high resistance to environmental factors and chemical compounds, ease of processing, aesthetics and good mechanical properties at a relatively low price. Unfortunately, polyester resins are also characterized by high flammability and intense smoking during combustion [2]. It is caused by, inter alia, high content of styrene used for their crosslinking. Therefore, in order to increase the safety of their use, they are modified with the use of different flame retardants [3-6]. Traditional micron flame retardants widely used for polyester resins include aluminum hydroxide (ATH), which was also used in the tested laminates. It is a mineral compound capable of releasing water molecules during the decomposition process. At temperatures above 200^0C aluminium hydroxide is split into aluminium oxide and water. The water cools the source of fire and thins the resulting fumes. Aluminium oxide forms a ceramic protective layer [3]. The flame retardants used must not only increase fire resistance but also limit the emission of dangerous fumes and toxic gases when burning of the composite material. The biggest smoke is generated by polymers, the decomposition of which is accompanied by the separation of condensed aromatic structures [4-9]. In rail transport, smoke emitted in the initial phase of fire is more dangerous than fire at this stage. Smoke makes it difficult to orientate passengers and causes panic, which creates problems with efficient evacuation. In addition, toxic decomposition products irritate the respiratory system and cause poisoning [2]. Therefore, in order to increase the safety of passengers in case of fire, all non-metallic materials used in European rolling stock must meet the requirements of EN 45545-2 [1]. This requirement also applies to the intensity of smoking and the content of selected toxic gases. A number of polyester resins have already been developed, which in laminates with a flame-retardant gel coat meet these requirements. Laminates based on these resins are, however, subjected to modifications in order to improve the stiffness of the products or reduce their weight and resin consumption. Laminates are also coated with paint coatings - this is aimed not only at changing the aesthetic properties of the products but also at improving their resistance to water.

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Laboratory tests

The purpose of the described work was to evaluate the effect of modification of vinyl ester-glass and polyester-glass laminates intended for rolling stock on their smoke properties during combustion. In the tested laminates, layers of rigid PVC foams, cork biocomposites and honeycomb layers were used as 'spacers'. Surface modification was also made by applying varnish coatings: Nuvovern WR Emaillack and MIPA coating.

The tests were carried out for laminates with a thickness of 10 mm made on the basis of two following types of resins:

-VE11M vinyl ester resin,

-Firestop 8175-W-1 polyester resin and Firestop S285 gelcoat.

Table 1 Marking and composition of the tested materials

Type of resin	Laminate composition	Marking of samples
vinyl ester resin VE11	9 x S600 – four-way glass fabric 600 $[g/m^2]$, vinyl ester resin VE11M	VE
	2 x gelcoat Firestop GC S714-2720, 9 x S600 – four-way glass fabric 600 $[g/m^2]$, vinyl ester resin VE11M	VE+2xG
	2 x gelcoat Firestop GC S714-2720 + 1 x S + CSM 900 – glass mat 300 $[g/m^2]$ + four-way glass fabric 600 $[g/m^2]$+ 1 x S600 – four-way glass fabric + Soric XF [6mm] – polyester synthetic layer + 2 x S600 – four-way glass fabric + vinyl ester resin VE11M	VE+2xG+S
	2 x gelcoat Firestop GC S714-2720 + 1 x S + CSM 900 – glass mat 300 $[g/m^2]$ + four-way glass fabric 600 $[g/m^2]$ + 1 x S600 – four-way glass fabric + Corecork 6 [mm] – cork biocomposite + 2 x S600 – four-way glass fabric + vinyl ester resin VE11M	VE+2xG+C
	2 x gelcoat Firestop GC S714-2720 + 1 x S + CSM 900 – glass mat 300 $[g/m^2]$ + four-way glass fabric 600 $[g/m^2]$+ 1 x S600 – four-way glass fabric +DIV 6 mm – PVC foam layer + 2 x S600 – four-way glass fabric + vinyl ester resin VE11M	VE+2xG+D
Polyester resin Firestop 8175-W-1	polyester resin Bufa Firestop 8175-W-1, gelcoat Bufa Firestop S270/, glass mat 150 $[g/m^2]$, glass fabric WR 600	R+G
	polyester resin Bufa Firestop 8175-W-1, gelcoat Bufa Firestop S285, glass mat (1x [150 g/m^2], 2x 450 $[g/m^2]$), topcoat Bufa Firestop S285.	R+G+T
	polyester resin Bufa Firestop 8175-W-1, 2 x gelcoat Bufa Firestop GC S714, 9 x S600 – glass fabric 600 $[g/m^2]$	R+2xG
	polyester resin Bufa Firestop 8175-W-1, gelcoat Bufa Firestop S285, glass mat (1x [150 g/m^2], 2x 450 $[g/m^2]$), topcoat Nuvovern WR Emaillack.	R+G+N
	polyester resin Bufa Firestop 8175-W-1, gelcoat Bufa Firestop S285, glass mat (1x [150 g/m^2], 2x 450 $[g/m^2]$), foam 25 [mm], topcoat Nuvovern WR Emaillack.	R+G+F+N
	polyester resin Bufa Firestop 8175-W-1, gelcoat Bufa Firestop S285, glass mat (1x [150 g/m^2], 2x 450 $[g/m^2]$), Coremat 5 [mm] topcoat Nuvovern WR Emaillack.	R+G+C+N
Polycarbonate	Lexan F2000	PC

For comparison, tests of smoke properties were also made for polycarbonate, which has high impact strength - it is difficult to break, and at the same time relatively light and could be successfully used for structural elements. However, it is currently impossible to use in rolling stock due to too high smoke emission during combustion.

The composition of individual layers of the tested laminates is shown in Table 1.

The measurements were carried out using a test stand for determining smoke intensity according to ISO 5659-2 [11] (Fig.1). For each individual specimen, the percentage value of light transmission was determined and the appropriate specific optical density was calculated on this basis. The results were reported in terms of D_s4 (optical density in first 4 min), and VOF4 (cumulative value of optical density in the first 4 mins - integral for the D_s4 curve in 4 mins).

Fig. 1. Smoke chamber according to ISO 5659-2 [11].

The results of the tests carried out for vinyl ester and polyester laminates modified with sandwich layers and paint coatings are presented in Tables 2 and 3 and in Figs. 2 and 3.

Table 2 Results of smoke intensity determination for vinyl ester based laminates and the values for polycarbonate.

Marking of samples (vinyl ester resin)	D_s4	VOF4
VE	629.17	955.4
VE+2xG	179.92	407.8
VE+2xG+S	234.6	478.1
VE+2xG+C	335.9	596.1
VE+2xG+D	254.6	584.4
PC	1070.1	1720

The introduction of modifications to the laminate structure based on vinyl ester resin resulted in a reduction of the amount of smoke emitted. The unmodified VE11M vinyl ester resin is characterized by high optical density values in the fourth minute of the D_s4 test. This parameter significantly exceeds the value of 300 which is, according to EN 45545-2 [1], the maximum acceptable limit for materials that can be used as lining elements (walls, ceilings) in European rolling stock. The VOF4 parameter is even more exceeded, where the permissible value according to EN 45545-2 [1] is 600. The most effective in terms of reducing the intensity of smoking turned out to cover the laminate with a double layer of the Firestop GC S714-2720 gel coat. In this version it meets the requirements of EN 45545-2 [1] in the field of smoke properties. Covering the gel coat resulted in the reduction of the Ds4 parameter over three times and the VOF4 parameter more than twice in relation to the unmodified laminate. A thick, airtight carbonized layer, fused with metal oxides of flame retardants, was formed on the surface of these samples. The formation of a protective layer on the surface of the sample can also change the release dynamics of the degradation products [5]. This process reduced the number of particles emitted in the gas phase [6]. Then the same laminate system was tested with three types of the following spacers:

- 6 mm synthetic spacer Soric XF synthetic polyester layer reducing weight, and through its structure optimizing the flow of resin between the layers - deterioration of the Ds4 parameter by 30% and VOF4 by 17% - the material meets the requirements of EN 45545-2 [1].
- 6 mm Corecork 6 mm spacer (it is a chipped, glued and then pressed cork oak bark layer, which has excellent insulating properties and resistance to acids and oils) - significant deterioration of smoke properties - Ds4 parameter increased by 87% and VOF4 46% - material no longer meets the requirements of EN 45545-2 [1],
- 6 mm foam spacer - PVC DIV (acoustic seals, anti-vibration primers, thermal insulation) - deterioration of the Ds4 parameter by 41% and VOF4 by 43% - nevertheless, the material meets the requirements of EN 45545-2 [1].

Table 2 Results of smoke intensity determination for polyester based laminates

Marking of samples (polyester resin)	D_s4	VOF 4
R+G	58.5	124
R+G+T	98.4	184.4
R+2xG	141.7	313.3
R+G+N	188.3	313.3
R+G+F+N	203.5	374.5
R+G+C+N	250.2	411.2

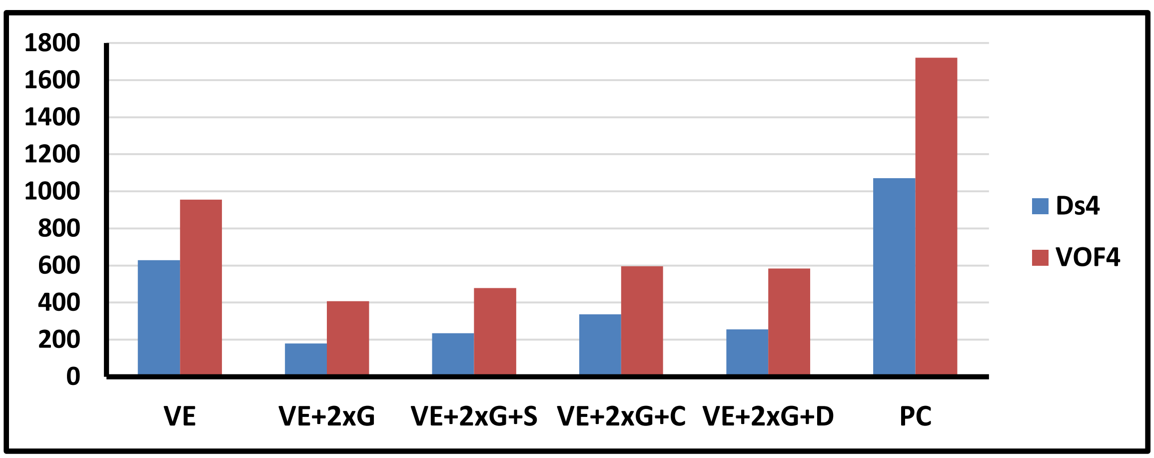

Fig.2 Values of the Ds4 and VOF4 after 4 mins. of tests for vinyl ester resin laminates and polycarbonate.

However, polycarbonate tested in the same conditions on samples with the thickness of 2 mm exceeded the upper limits of smoke parameters according to EN 45545-2 [1] in the following ranges:

- three times the value of parameter Ds4,
- almost three times the value of the VOF4 parameter.

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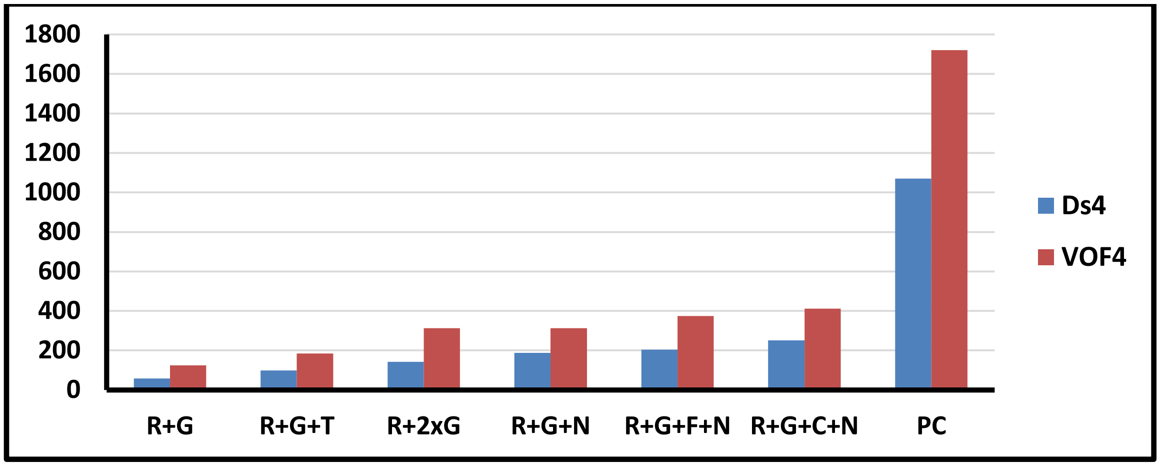

Fig.3 Values of the Ds4 and VOF4 after 4 mins. of tests for polyester resin laminates and polycarbonate.

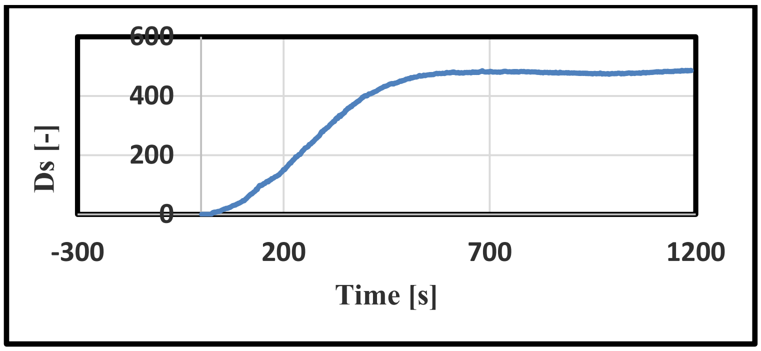

Fig. 4 Optical density in time for the GRP (resin Firestop 8175-W-1, with the Coremat layer)

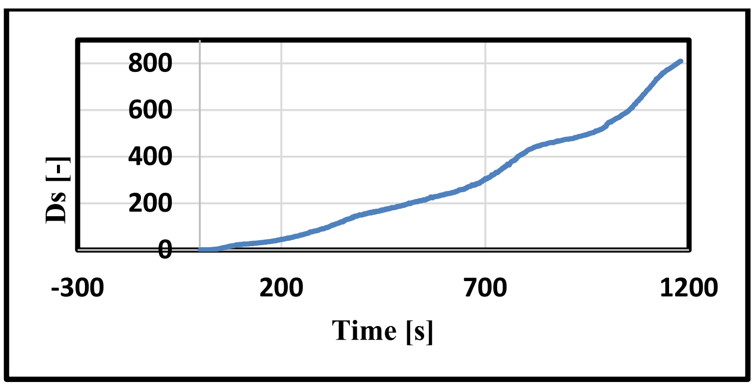

Fig. 5 Optical density in time for the GRP (resin Firestop 8175-W-1, no modification)

Based on the value of the VOF4 parameter, it is possible to assess how much smoke the burning material emits within the first 4 minutes of fire which are decisive for effective evacuation. For laminates based on the Firestop 8175-W-1 resins, the value of this parameter remains low, regardless of the method of laminate modification. The lowest value of the Ds4 and VOF4 parameters was recorded for the gel coat resin without modification. Further modifications by covering the laminate with a double gel coat, the Nuvovern WR Emaillack painting coating, adding a foam layer or the Coremat mat (improving the stiffness of the laminate, reducing its weight and resin consumption) have drastically reduced the smoke properties. The maximum increase in parameters took place for the laminate reinforced with the Coremat mat. The Ds4 parameter has increased by a factor of four

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and the VOF4 increased by more than threefold in relation to the unmodified base laminate. Nevertheless, the material still meets the requirements of EN 45545-2 [1]. The graph (Fig.4) shows an example of an optical density curve during the test for a laminate with the Coremat mat, which was characterized by the most intense smoke emission in the group of modified laminates based on the Firestop 8175-W-1 polyester resin. For comparison, in the next graph (Fig. 5) the optical density curve for the unmodified laminate, whose smoke parameters were at the lowest level in this group, is presented.

Summary

Smoke properties of composites based on polyester and vinyl ester resin in the base version and after the application of modifying layers were investigated. These modifications included covering with external coatings improving aesthetics, as well as introducing into the structure of composites materials that improve insulation properties, chemical resistance, and weight reduction. It was determined to what extent the improvement of functional properties influences the smoke parameters of these composites important from the fire safety perspective.

It has been shown that for laminates based on vinyl, ester resin coating with a double layer of flame-retardant gelcoat greatly reduces the amount of smoke emitted. On the other hand, other tested modifications worsened smoke properties. However, the introduction of the Soric XF layer or the PVC foam DIV increases the amount of smoke generated in such a range that the obtained values of the Ds4 and VOF4 parameters meet the requirements of EN 45545-2 [1]. On the other hand, in the case of laminates based on polyester resin, it has been shown that for each modification there is only a slight deterioration of the smoke properties and it is possible to use these composites in the rolling stock.

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