Introduction

Composite materials based on a polymer matrix and glass reinforcement are often used in transport vehicles. The main reasons for their utilization are their low mass, excellent formability and relatively low production costs for low and medium manufacturing series.

When composite and sandwich structures are used in train applications, they have to fulfill different requirements. The first (or the main) requirement is the fire safety. In addition to the fire safety of these materials, relatively high mechanical properties, dimensional and thermal stabilities and health safety are required. For example the French standard NF F01-28: Fiber reinforced plastic in railway rolling stock requires a minimum bending strength of reinforced plastics of up to 150 MPa, while maintaining the self-extinguishing properties according to another French standard, NF F16-101.

Polyester matrices reinforced with fiber reinforcements in various forms are primarily used for these applications. In these composite systems self-extinguishing properties are primarily achieved with additions of flame retardants to the synthetic matrices.

1 INTRODUCTION

Composite materials used in the transport industry and also in other sectors must have a certain degree of flame resistance. For this purpose, commonly used flame retardants are based on halogen compounds in the liquid state or aluminum hydroxide in the solid state. Solid flame retardants have a negative effect on the processing and mechanical properties. Low viscosity and rapid wettability of fibers are very important, especially in a resin transfer molding (RTM) process.

Therefore, a new advanced matrix system based on phosphorus flame retardants was developed. The flame resistance and mechanical properties of the composite materials produced from the new resin system were tested. Furthermore, the processing parameters and tests are described in the article.

Keywords: flame-retardant composites, phosphorus, RTM, vacuum infusion

1 INTRODUCTION

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on the viscosity of the resulting mixture, thus limiting their use in the preparation of a composite with the vacuum infusion or RTM technology. And, last but not least, they negatively influence the mechanical properties – the composites become less stiff and brittle.

They slow down the combustion process in different ways, physically or chemically. The physical processes include cooling the material, creating a protective layer (that continues to protect the remaining material, blocking the combustion by limiting the access of air) or diluting the gas flame with retardant components.

With respect to the chemical processes, flame retardancy is a reaction in the gaseous phase, leading to a release of significant amounts of water or carbon dioxide. Thus, a reaction at this stage limits and slows down a burning process. This group includes the flame retardants based on halogens. These compounds create carbon ash on the polymer surface or a swelling under the protective layer of the ash to provide a better thermal insulation.5

Some flame retardants based on halogens, such as polychlorinated biphenyls (PCB), or various brominated flame retardants (polybrominated diphenyl ethers, polybrominated biphenyls) may pose a health risk. The fire retardancy of a halogenated flame retardant is based on the formation of a volatile-combustion hydrobromic or hydrochloric acid in the presence of hydrocarbons (e.g., toxic dioxins) at a temperature of around 350 °C.

Flame retardants based on phosphorus are the compounds that are more environmentally friendly and their consumption is slowly growing. Phosphor flame retardants are already applied in matrices with phosphorus amounts of about 5–8 %. They work very well for the polymers containing oxygen in the chain.

2 EXPERIMENTAL WORK

2.1 Materials

2.1.1 Matrix

An unsaturated polyester resin diluted with styrene, containing a phosphorus flame retardant incorporated into the chain molecules was developed under the working title FR4/12 (Table 1). The goal was to prepare a resin, which enables, due to its viscosity, a preparation of the composite parts for rail vehicles using the RTM method or the vacuum infusion method. Pure resin would also meet the requirement for a flame resistance – the composites become less stiff and brittle.

Table 1: Mechanical and processing properties of FR4/12 matrix

<table>
<thead>
<tr>
<th>Material description</th>
<th>Matrix FR4/12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (Brookfield LV 2/12, 20 °C) (mPa s)</td>
<td>475</td>
</tr>
<tr>
<td>$T_{f}/^\circ C$</td>
<td>105</td>
</tr>
<tr>
<td>$HDT/ ^\circ C$</td>
<td>68</td>
</tr>
<tr>
<td>Acid number, the KOH content (mg g$^{-1}$)</td>
<td>2.5</td>
</tr>
<tr>
<td>Hydroxyl number, the KOH content (mg g$^{-1}$)</td>
<td>50</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>63</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>3400</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>2.2</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>3600</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>130</td>
</tr>
<tr>
<td>Oxygen index</td>
<td>32–34</td>
</tr>
</tbody>
</table>

2.1.2 Reinforcements, coatings

A multiaxial nonwoven fabric (bidirectional and triaxial fabric) was selected as the reinforcement. A nonwoven fabric guarantees a high proportion of glass in a composite (hence, better mechanical properties). It also has a suitable drapability. In line with the requirements of the process technology, mats with the trade name UNIFILLO ® were used for the RTM technology. To determine the effect of the coating on the combustibility, two samples of the BÜFA gelcoat layer were provided.

2.2 Production methods and testing

The testing of the resin system was carried out at two levels. One level was the production of the test samples. These samples were produced on a simple plate or in a simple RTM mold. The second level of the matrix testing consisted of a production of real products (prototypes). Production methods were chosen with respect to the environmental, health and economic aspects (productivity), including two closed-production technologies – VIP (vacuum infusion process) and RTM (resin transfer molding).

In addition to the newly produced matrix, a total of five composite materials (Table 2) of various compositions as well as other polymer systems were produced (Sample D was made from a phenolic prepreg, Sample E was based on a commercial matrix). Samples B and E were provided with a gelcoat. Firstly, the flexural test was realized according to ISO 178.7 With respect to the fire retardancy the oxygen index was recorded, and the tests of the flame spread and the (partial) heat release were performed using the cone calorimeter method.8,9

3 RESULTS AND DISCUSSION

The measured values of the mechanical properties and fire behavior are shown in Figure 1. As can be seen, the highest values for both flexural properties of the samples prepared with the wet technology were obtained.
for Sample C. Sample D prepared from prepregs showed excellent flexural performance and fire properties compared to the samples prepared with RTM and VIP; however, these materials are very expensive.

Moreover, comparing FR4/12 to the commercial matrix, it is obvious that the obtained mechanical properties are almost twice as high as for the samples prepared from FR4/12.

The tests of the fire properties (Figure 2) showed that the gelcoat layer also influences the flame spread and the heat release. Further, the oxygen index of Samples B (matrix FR4/12) and E (the commercial matrix) was the same for both samples. Sample C exhibited the lowest oxygen index of all the produced composites. Regarding the requirement for the oxygen index (higher than 30), all the samples passed the test. The heat-release parameter (Figure 3) was measured only for Samples A, B and C, where individual values were 211.6, 154.7 and 37.7. The curves in Figure 3 show the heat release during the combustion of the samples. The flame spread (Figure 4) for Samples A and C is the same (due to the same material composition).

4 CONCLUSION

The main objective of the mechanical testing was to determine whether the strengths of the material combinations reached 150 MPa (this value is the requirement...
of French standard NF F01-281). All the material combinations met this requirement with a certain safety margin, except for Sample E. The result was expressed with a high amount of the filler in the resin (the ratio of 1 : 1). It is obvious that after adding the additives the value of the bending strength decreases.

The objective of testing the fire resistance of the materials was to determine the level of the flame retardancy of the composites made from the new matrix system. Using a simple test – determination of the oxygen index – the materials could be classified into the mid-level category of flame-retardant resins. It was assumed that with the addition of non-reactive additives the oxygen index, together with the overall resistance to fire, would increase. According to all the flame-retardancy tests, the flame-retardant gelcoat plays an important role in improving the fire resistance.

The oxygen index (Table 3) for various composites based on the new matrix is very similar to the oxygen index of pure resin. Increasing the glass amount has a minimal impact on the oxygen index. However, it is assumed that with the additions of non-reactive additives to a composite system, the oxygen index will increase. The values of the heat release for the phenolic systems are relatively large in comparison with the values for the composite systems based on the new matrix.

The developed matrix exhibits excellent processing properties, good and fast fiber wetting, adjustable reactivity and curing times. Another advantage is that the used promoter is based on iron compounds.

From the overview of the properties of all the systems, it is clear that the polyester systems do not reach the same fire-resistance values as the phenolic systems. On the other hand, due to other advantages (surface quality, price and processing methods) the development of the composite systems based on polyester systems will dominate.

Acknowledgement

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