Fraunhofer
PYCO

FRAUNHOFER RESEARCH INSTITUTION FOR POLYMERIC MATERIALS AND COMPOSITES PYCO

New Fire Retardant Unsaturated Polyester Resins

From cone calorimeter experiment the following indicators can be achieved:

- Peak of Heat Release Rate (HRR_{peak})
- Maximum Average Rate of Heat Emission (MARHE)
- Total Heat Release (THR)
- Total Smoke Release (TSR)
- Char Residue (CR)

4: Burning sample inside the cone calorimeter

The main parameter for HL3-classification is MARHE. For HL3 the threshold value is 60 kW/m² and for HL2 (the lower FR-requirement) 90 kW/m². The required Hazard Levels (HL) depend on the type of train, e.g. HL3 will be required for underground traffic, long distance trains with sleepers and other types of trains.

	UP formulation	Content of ATH [phr]	Sample mass [g]	TTI [s]	HRR_{peak} [kW/m²]	MARHE [kW/m²]	THR [MJ/m²]	TSR [m²/m²]	CR [%]
Laminate 1	1	150	105	111	163	91	88	1320	66
Laminate 2	1	200	145	155	100	45	71	870	65
Laminate 3	2	100	118	82	138	78	84	2000	62
Laminate 4	2	150	147	152	134	55	81	1730	64
Laminate 5	3	150	134	113	140	63	96	1850	64
Laminate 6	3	200	196	161	103	43	123	1230	61
Commercial benchmark		300	117	149	114	53	58	326	62

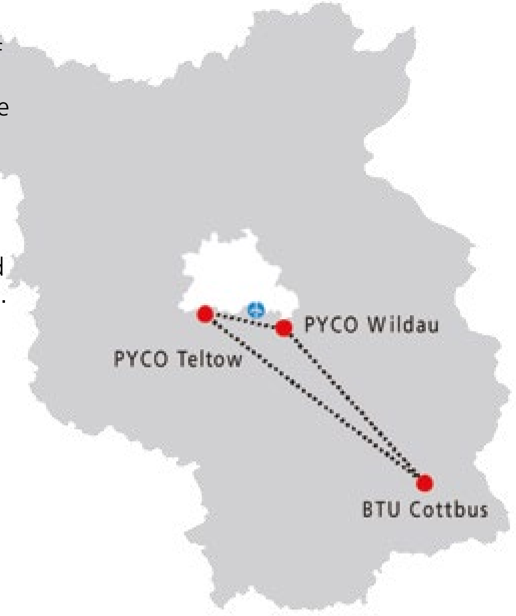
***5:** Cone-Calorimeter data for 10x10 mm²-samples at 50 kW/m² (TTI: Time To Ignition, HRR_{peak}: Peak of Heat Release Rate, MARHE: Maximum Average Rate of Heat Emission, THR: Total Heat Released, TSR: Total Smoke Released, CR: Char Residue, phr: Parts per Hundred)*

Technical Readiness Level (TRL)

The development has been patented and licensing is possible. All formulations are ready for technical implementation and market launch. Fraunhofer PYCO is able to provide samples up to 20 kg for processing and handling tests with costs covered by the buyer. The development has been patented and licensing is possible. All formulations are ready for technical implementation and market launch. Fraunhofer PYCO is able to provide samples up to 20 kg for processing and handling tests with costs covered by the buyer.

Location Berlin-Brandenburg

New solutions require new approaches: The locations of the research institute in Teltow and Wildau, where the metropolis of Berlin and the federal state of Brandenburg meet, offer optimal conditions for innovative scientific research.
Here, the products of tomorrow emerge from ideas and visions. Therefore, the institute's scientists have formed a creative research network with renowned universities, well-known large-scale enterprises, and various innovative medium-sized companies. Additionally, new synergy arises from the integration in the third largest location of aerospace industry in Germany.



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6: Main building

NEW FIRE RETARDANT UNSATURATED POLYESTER RESINS

Motivation

Fire safety is one of the most important challenges in public and individual transport. Especially the European standard CEN/TS 45545 for railway will demand a very high fire retardancy in different Hazard Levels (HL), depending on the type of train, for any material used in the future.
One of the most commonly used materials for railway applications are unsaturated polyesters. This broad applicable class of thermosetting composite material has only one big disadvantage - its good inflammability. Due to the new European standard the Unsaturated Polyesters (UP) are highly jeopardized for further use in railway infrastructure and rolling stock.

1: 20 kg condensation plant

Of course, today's unsaturated polyester resins and parts thereof are already fire retardant but in an unsatisfying manner.
Available commercial materials are highly filled with mineral fire retardants like aluminum hydroxide (ATH) or containing halogenated fire retardants.
While using a high filler amount the mechanical properties decrease and the density increases (unlikely for light-weight applications), the use of halogenated fire retardants is critically because of toxic and dangerous products in case of fire and they are already mostly banned from the market.
For this reason scientists at Fraunhofer PYCO have been investigating the mechanisms of fire retardancy and developed a highly fire retardant unsaturated polyester resin by using phosphorus containing building blocks for open mold application (hand lay-up / spray lay-up).

Resin Properties at a Glance

- Phosphorus content between 4 and 7 wt.-%
- Good and reproducible condensation properties
- Adjustable product properties by variation of the diols
- High content of building blocks from renewable resources are possible

GFRP-Properties at a Glance

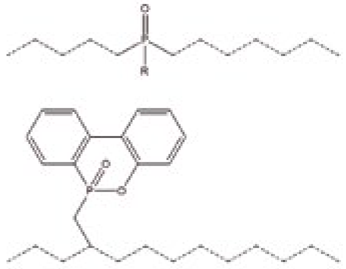
- High fire retardancy according to CEN/TS 45545-2 HL3 (MARHE)
- Low filler content (50-75 wt.-% less than commercial formulations)
- Good processing properties (wetting and degasing)
- Moderate curing activity
- Lamination of large parts possible
- Glass transition temperature up to 130 °C for UP3
- Post cure is recommended (2h @ 80 °C)

Intrinsic Fire Retardancy

The high fire retardancy could be achieved by using reactive phosphorus containing building blocks during the polycondensation process.
Intrinsic fire retardancy is advantageous in comparison to fire retardant additives, because many reactive and unreactive FR-additives lower the material or processing performance, while intrinsic fire retardant resins perform equally at any time and with or without a decreased amount of FR-additives.
Constraints for the phosphorus containing building blocks are:

- Good condensation properties
- Thermal stability
- Hydrolysis stability

All requirements could be observed for two very promising substances, but only by combination of both.
Disparity of both phosphorous compounds is the position of the phosphorus atom. The first compound is a phosphine oxide derivative with phosphorus bonded to the main backbone of the polyester.
The second phosphorous compound is a 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO) derivative with phosphorus in a side chain (see figure 2).
The combination of both compounds ends up in very good condensation properties for the resin production and a very high fire retardancy for molded parts.



Compound 1

Compound 2

2: Phosphorus position in Compound 1 and 2

Good balanced properties (fire retardancy, glass transition temperature and condensation properties) are obtained for a phosphorus content between 4-7 wt.-%.

Processing of the Resin

As reactive diluent a mixture of styrene and methyl methacrylate is used. The resin is designed for open mold applications.

Therefore the formulations are optimized for room temperature curing with Methyl Ethyl Ketone Peroxide (MEKP) together with cobalt salts as promoter. To obtain the highest performance a post cure at 80 °C is recommended.

To reach very high fire retardancy in laminates according to CEN/TS 45545-2 for instance a small amount of fire retardant mineral filler (ATH) is necessary. In comparison to commercial formulations the filler content is decreased by 50-75 wt.-%.

The filled and initiated resins show low viscosity, good wetting and degasing behavior and a moderate curing activity for lamination of larger parts.

Resin Formulations

Three different formulations with different properties are available. Formulation 1 shows the best processing properties and a moderate glass transition temperature (approx. 90 °C).

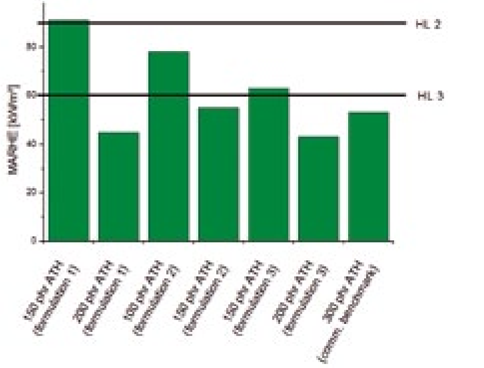
Formulation 2 considers 25 wt.-% of building blocks from renewable resources, a slightly higher viscosity than formulation 1 and a glass transition temperature slightly above 100 °C.

Formulation 3 has been developed for applications which require a higher thermal stability and shows a glass transition temperature (t_g) of 130 °C.

All formulations show comparable fire retardancies and can fulfill the requirements of HL2 and HL3 classification (see figures 4 and 5).

Cone Calorimeter

To investigate the fire performance of the new resin formulations a cone calorimeter was used. The CEN/TS 45545-2 requires cone calorimeter measurements for all materials inside and outside the train.



***3:** Maximum Average Rate of Heat Emission (MARHE) of different GFRP-laminates for 10x10 mm²-samples at 50 kW/m² (threshold value at 60 kW/m² for HL 3 and 90 kW/m² for HL 2)*

During the tests, the resin samples were exposed to a 50 kW/m² radiant heat flux.