Paper PATRAM 2019

For an oral presentation

Topic: Package Design (including Materials and Testing) **<u>OR</u>** Analysis (including Structural, Thermal, Shielding, Criticality, and Risk Assessment)

New Composite Materials for Neutron Protection

Author: Constance ROBEYNS

Keywords: Neutron-shielding materials, composite, boron, resin, radioactive material storage

Introduction

The protection against radiations, gamma and neutrons, is an essential parameter in nuclear industry development. Since the 70s, ROBATEL Industries company designs and products transportation packages for highly radioactive materials. Neutron and thermal protection materials are used in those packages to catch neutrons and to limit the increase of temperature in case of fire. These composites are made of a cement-based matrix, plaster-based matrix or resin-based matrix with mineral or organic fillers. Once the neutrons have been slowed down by the hydrogen contained in the composite, a mineral filler enables the neutron capture thanks to its high content of boron.

These materials are usually limited in their “normal use” temperature range due to their organic components or by the presence of water in the concrete of plater base.

Therefore, to increase the maximal temperature of normal use and in the same time to increase the neutron shield efficiency, new materials called Compound 23™ and Compound 24™ have been designed in ROBATEL Industries laboratories. Those materials are epoxy resin-based composites. Different formulations were tested to mitigate the fillers segregation phenomenon, or to avoid a too long curing time. Fire retardancy properties were also investigated in the case of Compound 24™. Finally these composites have been characterized and mechanically tested.

I. Synthesis of Compounds 23™ and 24™

The two new materials must fit some characteristics, especially the neutron-shielding properties.

Compared with other neutron-shielding materials developed by ROBATEL Industries, such as PNT7™ or Compound 22™, the Compound 23™ and Compound 24™ must show a higher hydrogen content (H > 9wt%) for fast neutrons, and higher boron contents too (B > 0.8wt%). and the normal operating temperature should be 160°C, with a transient operating temperature of 200°C and maximum accidental temperature of 240°C.

The casting time should be inferior to 24h with no segregation of charges.

Materials

The matrix used to prepare the Compounds is an epoxy resin (ER), a hardener (H) and fillers to bring the boron and the fire resistance.

Several thousand R&D hours were necessary to obtain the two compounds with the wanted properties, especially the ageing of materials and the resistance against fire for CP24™.

Results

The Compound 24™ color is dark grey (rhino grey), while it is piano black for Compound 23™. Densities for CP23™ and CP24™ are 1,2 g/cm^3 and 1,4 g/cm^3, respectively.

II. Mechanical tests on the Compounds

After the researches and experiments to avoid the segregation of charges during the fabrication of Compound 23, the compounds could be tested in order to know their mechanical properties.

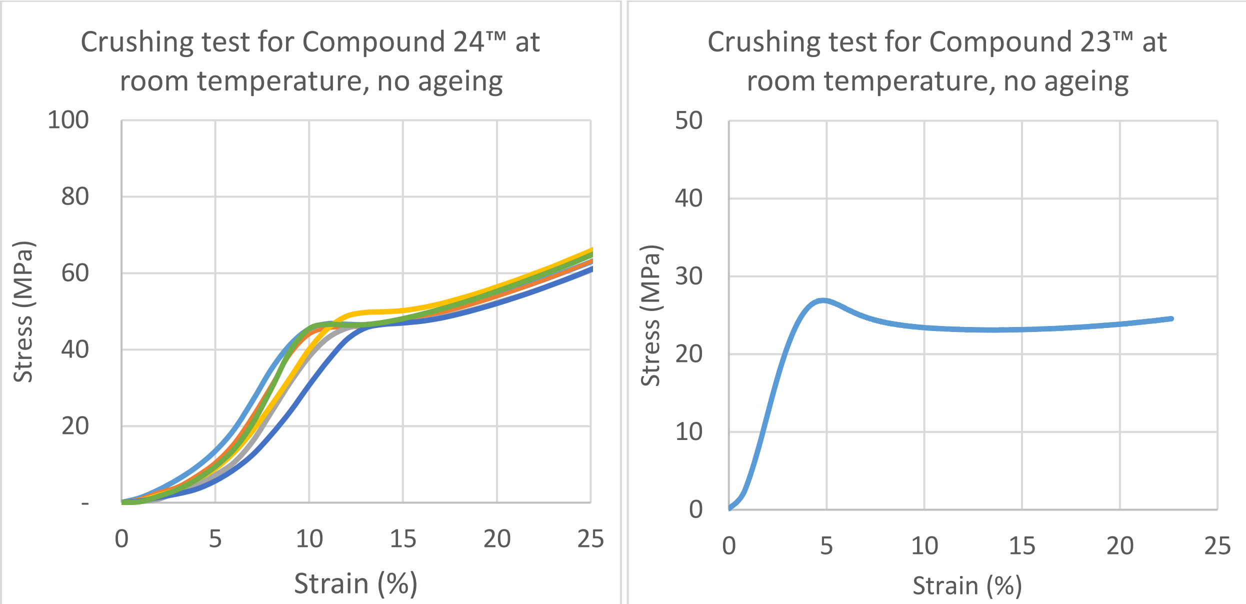
Test procedure follows the norm NF EN 196-1. The dimensions and mass of each sample is measured before testing. The crushing machine was an AGS-X 300 Shimadzu, with a capacity of 300 kN and a strain precision of 0.01 mm. The force is measured with a precision of 0.5% of the value.

The stress at break is calculated based on the limit force before breaking following the equation:

$$R_c = \frac{F_c}{S}$$

Where F_c is the force at breaking (in N), S is the surface of the sample (in mm²).

The crushing tests are run at room temperature with no thermal ageing. Stress-strain curves are plotted in Graph 1.



Graph 1: Stress-strain curves of Compound 24™ (left) and Compound 23™ (right) at room temperature, with no ageing.

Results show maximum stress before the "shoulder" around 45 MPa for CP24™ and 26 MPa for CP23™.

Figure 1: Pictures of Compound 23™ sample after crushing

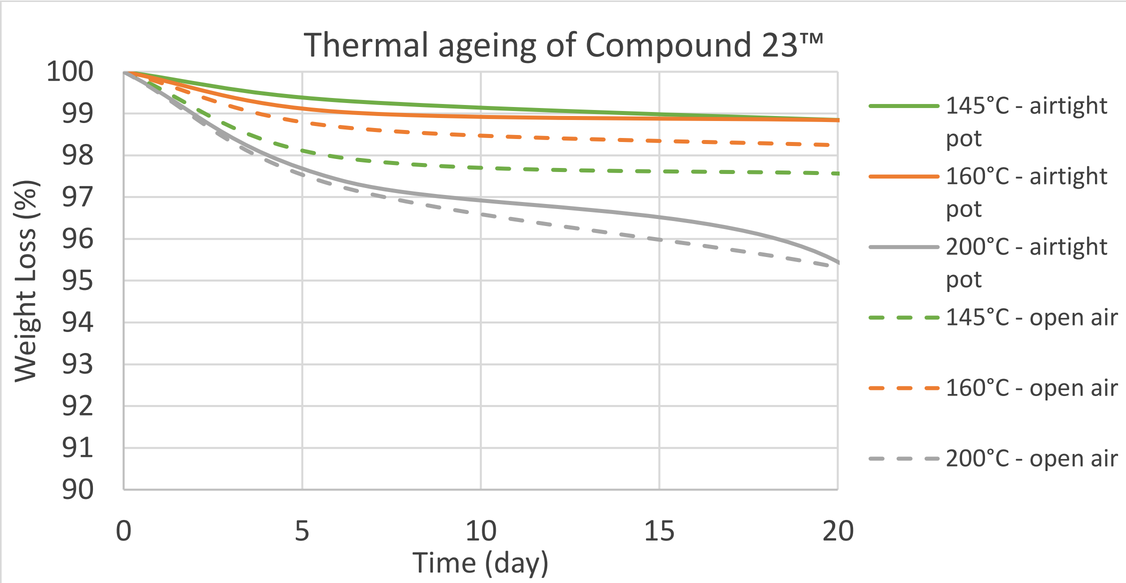
III. Thermal properties

Samples ageing

Samples of Compound 23™ were aged at different temperatures for different periods of time, and their mechanical properties were investigated. For each temperature-time setting parameter, a sample was left in open air while another was inserted inside an airtight pot. Ageing time is at least 45 days and can be up to 160 days.

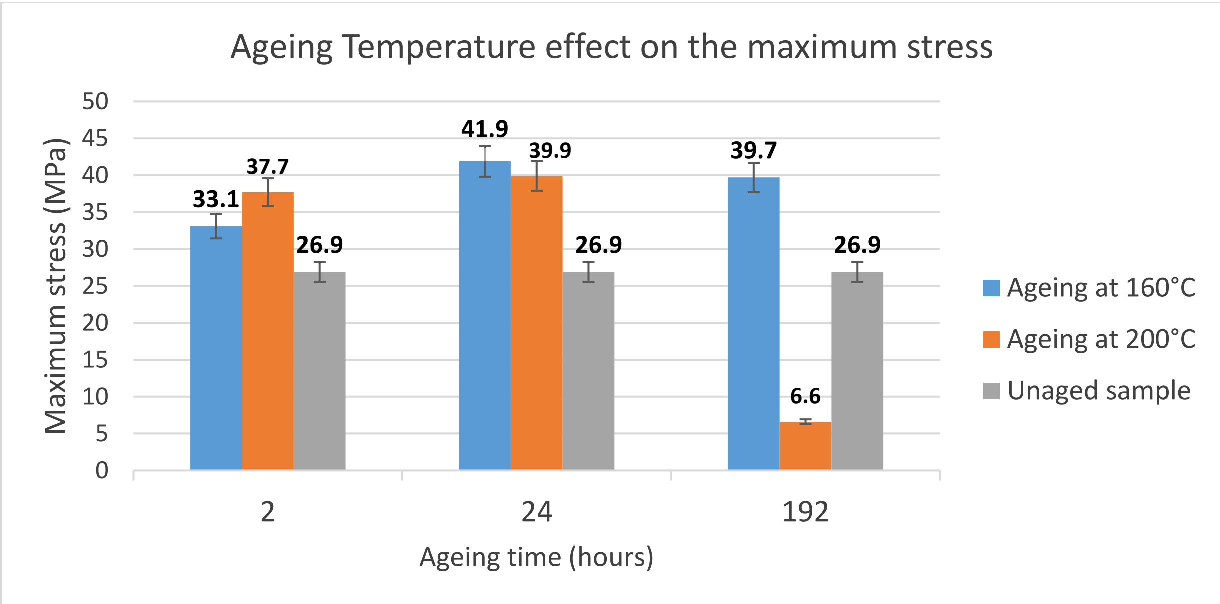
At 130°C, 145°C and 160°C, the dimensions of all samples (in open air or in airtight pots) remained unchanged.

The measure of weight loss with time was plotted for both samples in open air and in airtight pots, see Graph 2. We can observe that confined samples didn't significantly lose weight: after 20 days, samples at 145°C or 160°C lost about 2% of their original mass, and this weight loss is stable until the end of our experiment (160 days). At 200°C, weight loss reached 5% after 20 days for both confined and free samples. Therefore, confined Compound 23™ can stand 200°C for a short period of time, which makes it an interesting composite materials for a use in environments subjected to high temperature for a short period of time.



Graph 2: Evolution of mass loss with time and temperature for samples of Compound 23™ in airtight pots and in open air.

Mechanical properties of aged samples were also investigated. The maximum stresses for crushing tests at room temperature were compared between samples aged at 160°C and 200°C. Unaged samples are also tested for comparison, and results are shown in Graph 3.



Graph 3: Ageing temperature and time effects on the maximum stress at room temperature.

High temperature ageing stiffened the compound but degraded it simultaneously. An ageing at 160°C or 200°C for at least 2 hours made the Compound 23™ more rigid than the unaged sample. This thermal treatment stiffened the materials, but an aging for longer time (192 hours) at 200°C induced a significant decrease in the maximum stress.

Fire resistance

The resistance against fire was tested on Compound 23™ and Compound 24™ following the UL 94 flammability ratings. If the final formulation of Compound 23™ doesn't make it totally fire-proof, the formulation of Compound 24™ was determined in order to make it fire-resistant. A parallelepiped sample was horizontally burned (HB) and had its extremity (the first 25 mm) in a flame for 5 min. The burning rate was under around 5 mm/min, which is lower than 75 mm/min (values from the UL 94 ratings) and the burning stopped before 100 mm, no drips of particles were observed. Then another test was run, but this time the sample was vertical. The burning stopped within 10 seconds and no drips of particles were seen. Therefore, the Compound 24™ is classified V-0.

Thermal conductivity

The thermal conductivity of both compounds were measured with the HotDisk method, on several samples for reproducibility. Values for CP23™ and CP24™ are respectively 0,22 and 0,77 $W.m^{-1}.K^{-1}$. The difference between the compounds is due to the variation of both fillers type and content. Knowing the density of these compounds, their heat capacity could be calculated, and shown in Table 1 where the other properties are summarized.

Table 1: Specification for the design of the new compound 23™ and compound 24™.

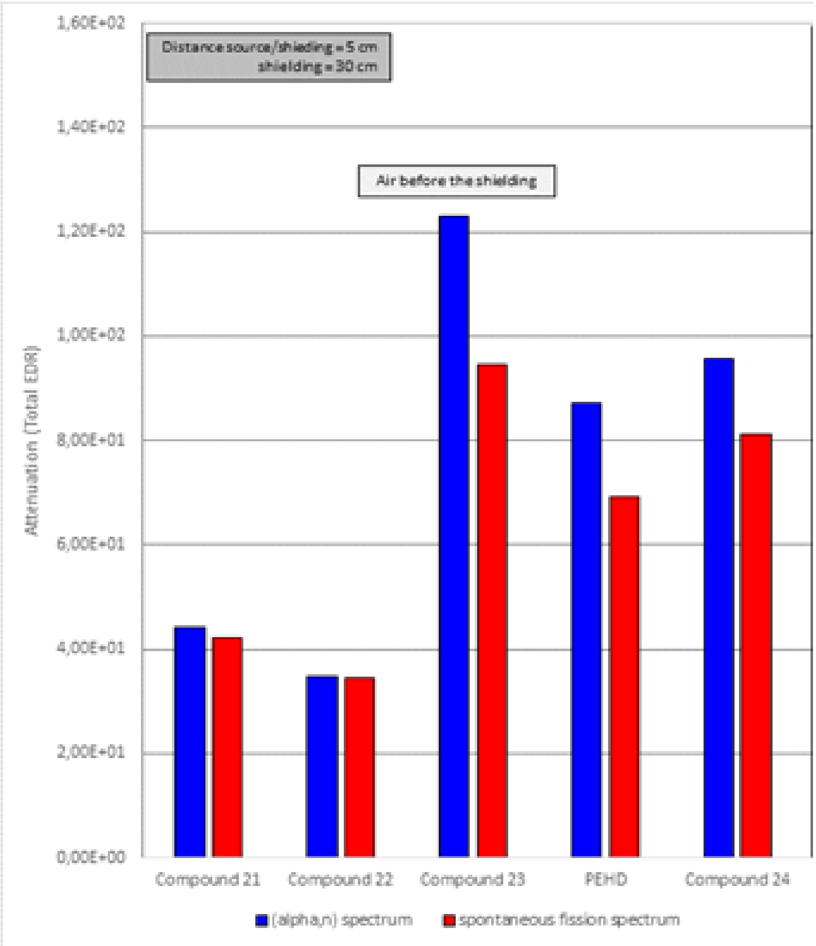
	CP23™	CP24™
Hydrogen concentration	9,8 %	6,5%
Boron concentration	2,6%	5,2%
Density	1,2 g/cm^3	1,4 g/cm^3
Thermal conductivity	0,22 ± 0,01 $W.m^{-1}.K^{-1}$	0,77 ± 0,02 $W.m^{-1}.K^{-1}$
Heat capacity	1760 ± 180 $J.kg^{-1}.K^{-1}$	1550 ± 160 $J.kg^{-1}.K^{-1}$
Limit temperature (normal use)	130°C	130°C
Limit temperature (accidental use)	200°C	200°C
Stress at break (20 °C)	26 MPa	45 MPa

IV. Comparison with other ROBATEL Industries materials

Neutron shielding

One interesting characteristic of Compounds 23™ and 24™ are their boron and hydrogen contents. Indeed, compared with other materials made by ROBATEL Industries, they bring an additional protection against slow and fast neutrons. Boron content is 2,6 % and 5,2% for CP23™ and CP24™, respectively, while it is only 0,9% for Compound 9™ and around 0,8% for both CP21™ and CP22™.

In order to represent the improvement in neutron shielding properties, simulations were run and compared with PEHD, as shown in Graph 4. It is clear from this graph that Compound 23™ and Compound 24™ bring a higher neutron shielding in addition to interesting temperature range for using.



Graph 4: Attenuation of different materials in air.

Using temperatures

As we saw previously, the normal operating temperature is around 160 °C for Compound 23™ and Compound 24™. As a comparison, it is 100°C for Compound 21™, 130°C for Compound 22™ and 120°C for PNT7™. Maximum accidental temperature is also higher than for other compounds, the exception is for PNT7™ that is a cement-based materials and therefore can withstand pretty high accidental temperatures (up to 800°C).

Conclusion

In order to bring new neutron-shielding materials on the market, Research & Development department in ROBATEL Industries imagined new hydrogen-enriched formulations of epoxy-based composites. Compound 23™ and Compound 24™ show interesting hydrogen and boron contents, as well as improved thermal properties and good mechanical properties (Table 1). Once commercialized, these composites could be used in the conception of neutron shielding plugs, hot cells, doors, tiles and so on.

The other interest with these two materials is the possibility to change their boron rate, in order to customize even more the neutron-shielding properties of these new materials.