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Does age matter? Impact on fire safety properties of composite materials from ageing

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Abstract. When materials are tested and classified before entering the market, they are mainly tested as newly produced. However, it is known that material properties change with time and when exposed to temperature, humidity, wind and light. As a result, it is important to have knowledge of how material age and which parameters are affected in order to retain safety. Studies show how the mechanical properties change when the materials age. But not much can be found in literature about the ageing effect on fire properties. In the present study, accelerated ageing testing was made with a composite material of phenolic resin and basalt fibres. Selected ageing methods applied were thermal ageing at 90 °C and moisture ageing at 40 °C and 90 % Relative Humidity. Samples were collected from ageing chambers after one, two and four weeks. To investigate the ageing effect on the fire properties of the composite, fire testing was conducted using cone calorimetry according to ISO 5660-1. The test results showed that ageing does matter. There was an impact on the material and the fire properties were affected. The ignition time decreased for the aged samples and the heat release rate slightly increased. Also, the smoke production increased with ageing.

1. Introduction

When new products and materials are fire tested and classified before entering the market, they are tested as newly produced. However, it is known that material properties change with time and when exposed to harsh environments such as elevated temperature, humidity, wind and/or light. Many studies in literature show how mechanical properties change and deteriorate when the materials age. Not much can be found in the literature on the ageing effect on fire properties. An important question is what happens with fire properties when materials are exposed to temperature and humidity for a long time [1].

Composite materials are widely used in applications in ships, railway vehicles, wind turbines and construction. Fibre Reinforced Polymer (FRP) composite materials are lightweight and have good mechanical properties. However, their weakness is the fire behavior, since they are combustible they will burn, and this can harm the safety of the construction [2]. For composite materials to be more resistant to fire there is often a treatment applied with flame retardants. The flame retardants can be added to the materials surface, mixed with the material or incorporated in the material chemically. As confirmed by fire testing of newly produced materials, the criteria for fire performance are achieved. However, how these flame retardants act when aged is to a large extent unknown [1].

With respect to maintenance and the sustainable life cycle, it is essential to know the time for replacement of materials in applications such as vehicles and buildings due to degradation in the material. It is critical to know at what stage the material no longer fulfils the safety regulations and



requirement regarding the fire safety. From an environmental perspective, the replacement of materials should not be done too early in a products life cycle. Altogether, the ageing effect on material properties is important.

2. Theoretical background

The only truly valid ageing method is storing materials for the corresponding time in their end use climate and then evaluate the material properties. However, this is time consuming and often not an option in development processes. Accelerated ageing can be used in order to shorten the process, which is a method to expose materials to a proper simulation of long-time use. Damage and degradation of the material can occur after a few days, weeks or months, which would normally occur after years of use in end use climate [3] [4].

2.1. Accelerated ageing methods

The selection of ageing method is important and should represent the end use climate. Important parameters to consider when selecting ageing method are the time scales, number of experimental points, choice of degradation agent and parameters to evaluate. The degradation agents are light, heat, liquids, gases, radiation, mechanical stress and electrical stress. The degradation of materials can be both physical and chemical. If the selected ageing method or climate is too tough, there can be a physical degradation or chemical reactions which would not take place when the materials are aged in real-time with end use climate. This will result in an incorrect evaluation of the material properties [3] [5]. In the following sections, thermal and moisture ageing are described more closely as they were applied in the current work.

2.1.1 Thermal ageing. Thermal ageing is a commonly used accelerated ageing method which is easy to conduct. The impact of thermal ageing with a polymer is molecular impairment within the material due to exposure of heat. As a result, the long polymer chains are broken and reactions are initiated, leading to a change in material properties [6]. Degradation mechanisms of a FRP composite material is temperature dependent and the degradation increases with increasing temperature [1]. In this paper, thermal ageing is the exposure to an elevated temperature during a discrete time.

A useful tool to correlate the time for accelerated ageing with actual ageing time in the end user application is the Arrhenius Rate Law, defining the rate of a chemical reaction as increasing exponentially with the absolute temperature. The Arrhenius Rate Law is given by equation (1).

$$\ln k(T) = -\frac{E_a}{RT} + \ln A \quad (1)$$

Where k is the reaction rate of the process, E_a is the activation energy, R the universal gas constant, T the absolute temperature and $\ln A$ is the pre-exponential factor, expressing the total number of molecular collisions that may initiate a reaction [3]. High temperature and low activation energy results in a higher rate constant speeding up the degradation process [7] [5]. Thus, when a material is exposed to higher temperature the speed of chemical reactions in the material increases. This increase in kinetic energy of the molecules is described by RT in the Arrhenius rate law. If the reaction mechanism does not change with temperature the activation energy is constant. When dealing with an activation energy independent of temperature, there is a linear relationship between the logarithm of the reaction rate, $\ln k$, and the inverse of the absolute temperature. This can be simplified with a rule of thumb for reactions at room temperature; the reaction rate doubles for every 10 K increase in temperature. If a material is stored at 30 °C for 10 weeks, the accelerated ageing climate corresponding would be 40 °C for 5 weeks. However, care should be taken with extrapolations [8] [9].

2.1.2 Moisture ageing. A high moisture content constitutes a harsh environment for many materials since it can cause damage to the material structure. The material can absorb moisture resulting in dimensional changes, swelling, reduction in glass transition temperature and/or reduction of mechanical properties [2] [10]. Accelerated ageing with moisture can be conducted in numerous ways. It can, e.g., be exposure to a specific humidity of the surrounding atmosphere or by immersion in a liquid [3] [10].

3. Experimental method

The materials used and the methods of fire testing of the aged and unaged materials are presented below.

3.1. Material

An FRP composite material consisting of Phenolic resin and Basalt fibres was used for the study. This material could, e.g., be used in wall or floor applications inside a ship or as windmill rotors. This composite also contained an expansion agent which is active during manufacturing of the composite, and its mechanism gives the possibility for different densities of the composite. The selected composite for the study had a density of 1000 kg/m³ and a thickness of 3 mm.

3.2. Accelerated ageing

The intended end use of the Phenolic/Basalt composite material investigated in this study is an application as a wall or floor kept at 20 °C for at least 10 years. Using the rule of thumb of Arrhenius Rate law this would correspond to an accelerated ageing climate exposure of 90 °C for 4 weeks. Samples were taken from the heat chamber after one week, two weeks, as well as four weeks, in order to follow the expected degradation of the material. However, since 90 °C is a considerable higher temperature compared to the end use climate, there is a possibility that non-typical reactions can occur due to the high temperature, which would not occur when aged in real-time. This would not be possible to exclude without conducting ageing tests for longer times at lower temperatures.

For this study, moisture ageing with a specific air humidity was selected. The Phenolic/Basalt composite material was aged at 40 °C and with a Relative Humidity (RH) of 90 %. Samples were collected from the humidity chamber after one week, two weeks and four weeks [11] [12].

3.3. Testing with TGA

To evaluate the thermal stability of the Phenolic/Basalt composite material, Thermal Gravimetric Analysis (TGA) was applied. During this test, the mass of the material was monitored over time as the temperature increased with 10 K/min. Tests were conducted with ambient air as the atmosphere [13].

3.4. Fire testing

Fire testing was conducted using cone calorimetry according to ISO 5660-1 to measure time to ignition and heat release rate (HRR). The samples were mounted horizontally and exposed to a heat flux of 50 kW/m². Duplicate tests were run with unaged samples and samples aged for one week, two weeks and four weeks. The test duration was 20 min [14].

When conducting cone calorimeter tests with composite materials, there is often unwanted burning originating from the specimen edges. This results in an extra contribution in heat release to the test results which would not appear in the end use of the product. To avoid this edge effect, a modified specimen holder was used. The sample specimen had the size of 136×136 mm and a modified frame with a circular opening with a diameter of 106 mm was used. This resulted in an exposed area of the specimen that was the same as that of the standard specimen holder described in ISO 5660-1. The larger distance to the specimen edges in the modified specimen holder was intended to prolong the time until start of pyrolysis of the edges. Further, between the sample and the retainer frame of the specimen holder was a 5 mm thick slab of insulation to prevent heating of the unexposed surface [15].

4. Results

Results from the tests conducted are given below. The aged samples were compared to unaged samples regarding physical appearance by visual inspection and fire safety properties by the cone calorimeter tests.

4.1. TGA test results

The results showed a relatively small gradual mass loss up to 300 °C and can therefore be seen as thermally stable at temperatures below 300 °C. Above this temperature, significant thermal degradation took place. Based on these results, using an accelerated ageing temperature of 90 °C, would be acceptable since it is below the critical temperature.

4.2. Visual inspection

A visual inspection was made of all samples after the accelerated ageing. The samples exposed to heat showed a distinct colour change. This colour change occurred already after one week. There were no shrinkage or mass change. The samples exposed to moisture and moderately increased temperature showed some colour change, not as distinct as for the thermally aged samples. There were no shrinkage or mass change.

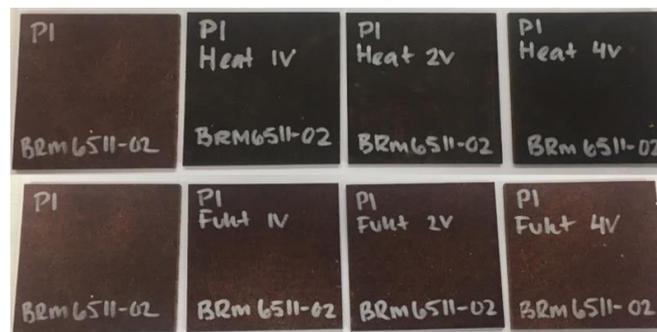


Figure 1. Samples of Phenolic/Basalt composite after thermal ageing (upper photo) and moisture ageing (lower photo). The sample to the left is unaged, then to the right, samples aged for one week, two weeks and four weeks, respectively.

4.3. Cone calorimeter testing

Table 1 shows the results of duplicate tests conducted with the cone calorimeter for unaged and thermal aged samples. Both the unaged samples and samples aged for one week show good repeatability regarding time to ignition and Total Heat Release (THR). The peak Heat Release Rate (HRR) has somewhat lower repeatability. However, the Total Smoke Production (TSP) shows very low repeatability, the value is about twice as high for one of the duplicates in both cases. The repeatability of the samples aged for two and four weeks was less good in case of time to ignition and especially peak HRR. One can note that for both the two- and four-weeks aged samples, the duplicate test with the longest time to ignition showed a higher peak HRR. The repeatability of TSP was better for the two- and four-weeks samples.

Visual observations in the tests showed the same general burning behaviour for all thermal aged samples as well as for the unaged samples. Early in test, before ignition of sample, there were a loud popping sound (from delamination) and flashing from the surface. All samples showed smoke appearing from the rear side of the specimen holder (from edge leakage of pyrolysis gases), but no ignition. The time for smoke at the rear side varied for the samples. For the unaged samples, smoke from rear side was observed at 170-200 s. This observation was noted at an earlier time for the aged samples, at 50-70 s for the one-week aged samples, at 120-170 s for two weeks aged samples and at 110 s for the four weeks aged samples.

Table 1. Cone calorimeter results of thermally aged material, duplicate tests.

Ageing time	Time to ignition (s)	Extinguished at time (s)	peak HRR (kW/m ²)	THR ₃₀₀ (MJ/m ²)	THR (MJ/m ²)	TSP ₃₀₀ (m ² /m ²)	TSP (m ² /m ²)
Un aged	93	726	110	12	35	85	87
	96	735	135	13	35	161	161
<i>mv (rel md %)</i>	<i>95 (2)</i>	<i>731 (1)</i>	<i>123 (10)</i>	<i>13 (4)</i>	<i>35 (0)</i>	<i>123 (31)</i>	<i>124 (30)</i>
1 week	62	835	87	11	33	41	52
	59	651	107	12	33	82	99
<i>mv (rel md %)</i>	<i>61 (2)</i>	<i>743 (12)</i>	<i>97 (10)</i>	<i>12 (4)</i>	<i>33 (0)</i>	<i>62 (33)</i>	<i>76 (31)</i>
2 weeks	84	813	190	16	40	206	221
	68	918	130	15	39	180	191
<i>mv (rel md %)</i>	<i>76 (11)</i>	<i>866 (6)</i>	<i>160 (19)</i>	<i>16 (3)</i>	<i>40 (1)</i>	<i>193 (7)</i>	<i>206 (7)</i>
4 weeks	73	699	112	14	37	120	121
	88	997	153	15	39	177	187
<i>mv (rel md %)</i>	<i>81 (9)</i>	<i>848 (18)</i>	<i>133 (15)</i>	<i>15 (3)</i>	<i>38 (3)</i>	<i>149 (19)</i>	<i>154 (21)</i>

Note: *mv* is the mean value of the duplicate tests and *rel md %* is the relative mean deviation in percentage from the mean value.

Despite the in some cases low repeatability of the duplicate tests, some valid conclusion can be made. The results showed clearly that the reaction-to-fire properties were affected by the ageing conditions. There was a faster ignition of all thermally aged samples compared to unaged samples. The HRR as a function of time of all samples are shown in Figure 2. The peak HRR decreased for samples aged for one week compared to the unaged samples, but the THR did not change. The THR value presented in Table 1 show the total heat release from ignition to end of test. As shown in Figure 2, the HRR reaches a steady-state production at approximately 300 s which gradually slowly decreased until the time of extinguishing. In addition, the total heat release was calculated from time for ignition to 300 s of test time, THR₃₀₀. This shows that even though the peak HRR for the one-week aged samples was lower than for the unaged samples, the total heat release from the samples was the same. Samples aged for two and four weeks showed an increase in the peak HRR compared to the unaged samples. The THR₃₀₀ also showed an increase for the two- and four-weeks aged samples, as well as the THR for the complete tests.

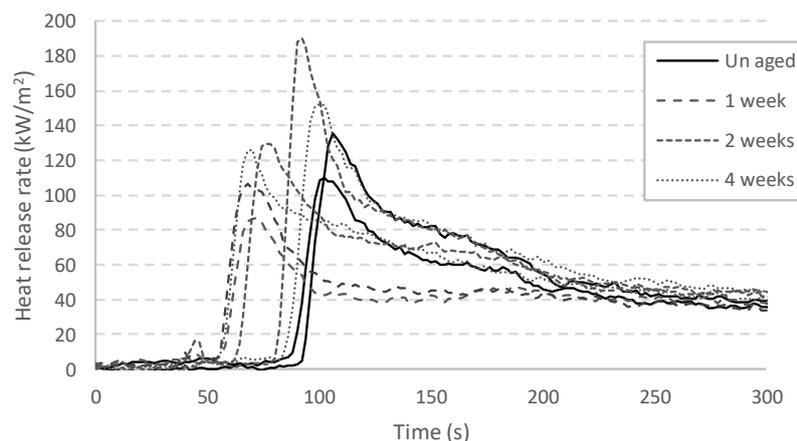
**Figure 2.** Heat release rate as a function of time, thermally aged material, duplicate tests.

Figure 3 shows the smoke production rate as a function of time. The smoke production increased fast at time for ignition, shown by the peak, and then decreased slowly. After 200 s, the smoke production had decreased for all samples, to stabilize close to zero. Table 1 shows the result of TSP₃₀₀, total smoke

production from ignition to 300 s of test, and TSP, total smoke production from ignition to end of test. The repeatability of the smoke results was poor in the duplicate tests with the unaged and one-week aged samples as already discussed. The repeatability of TSP was better for the two- and four-weeks samples, and it is clear from the results that more smoke was produced from these samples compared with the unaged and one-week aged samples.

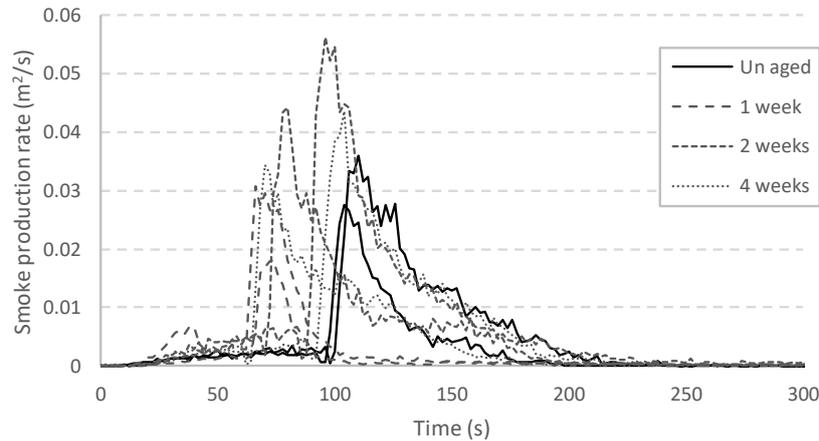


Figure 3. Smoke production rate as a function of time, thermally aged material, duplicate tests.

Table 2 shows the cone calorimeter results of the unaged samples and samples exposed to moisture and moderately increased temperature. The repeatability of the duplicate tests was acceptable for all test parameters with exception of the smoke production for the unaged samples.

Observations made during the tests showed a similar burning behaviour for both unaged samples and aged samples. Before ignition of the sample there was the loud popping sound as mentioned earlier. All samples showed smoke leakage from the rear side of the specimen holder, but no burning. Time for the smoke observation was at 170-200 s for the unaged samples as discussed above, 100-140 s for one-week moisture aged samples, 170-240 s for two weeks aged samples and 140-230 s for four weeks aged samples.

Table 2 Cone Calorimeter results of moisture aged material, duplicate tests.

Ageing time	Time to ignition (s)	Extinguished at time (s)	peak HRR (kW/m ²)	THR ₃₀₀ (MJ/m ²)	THR (MJ/m ²)	TSP ₃₀₀ (m ² /m ²)	TSP (m ² /m ²)
Un aged	93	726	110	12	35	85	87
	96	735	135	13	35	161	161
<i>mv (rel md %)</i>	95 (2)	731 (1)	123 (10)	13 (4)	35 (0)	123 (31)	124 (30)
1 week	97	930	146	14	36	198	205
	98	617	149	13	36	171	172
<i>mv (rel md %)</i>	98 (1)	774 (20)	148 (1)	14 (4)	36 (0)	185 (7)	189 (9)
2 weeks	100	721	156	15	39	234	247
	100	753	163	15	38	222	228
<i>mv (rel md %)</i>	100 (0)	737 (2)	160 (2)	15 (0)	39 (1)	228 (3)	238 (4)
4 weeks	97	784	148	15	41	234	239
	106	828	148	14	37	185	186
<i>mv (rel md %)</i>	102 (4)	806 (3)	148 (0)	15 (3)	39 (5)	210 (12)	213 (12)

Note: *mv* is the mean value of the duplicate tests and *rel md %* is the relative mean deviation in percentage from the mean value.

Comparing the test results of the unaged samples with the moisture aged samples shows that the accelerated aging had some limited effect on the reaction-to-fire properties. There was a slight increase in time to ignition for all aged samples. There was also an increase in peak HRR for all aged samples, with highest peak for the two weeks aged samples, shown in Figure 4. The heat release decreased after the initial peak at time for ignition, to reach a steady state of heat release at approximately 300 s. The THR increased somewhat with increasing ageing time for all aged samples compared to the unaged samples.

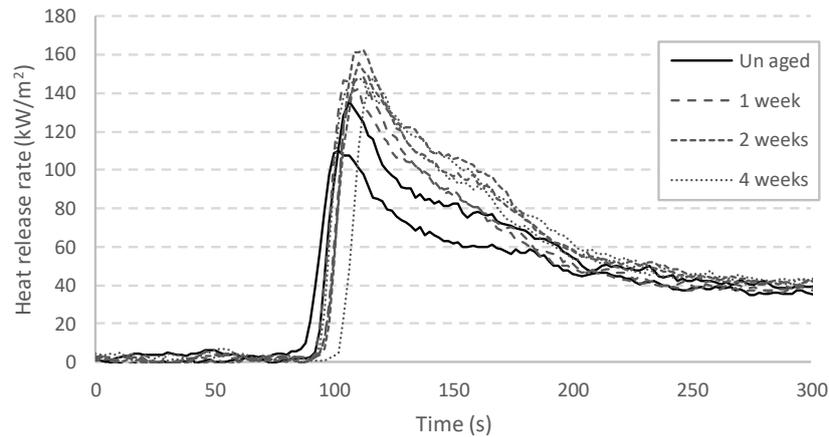


Figure 4. Heat release rate as a function of time, moisture aged material, duplicate tests.

The smoke production rate shown in Figure 5 illustrates that all aged samples had a higher smoke production compared to the unaged samples. All samples showed a peak in production at time for ignition followed by a decrease to almost no production.

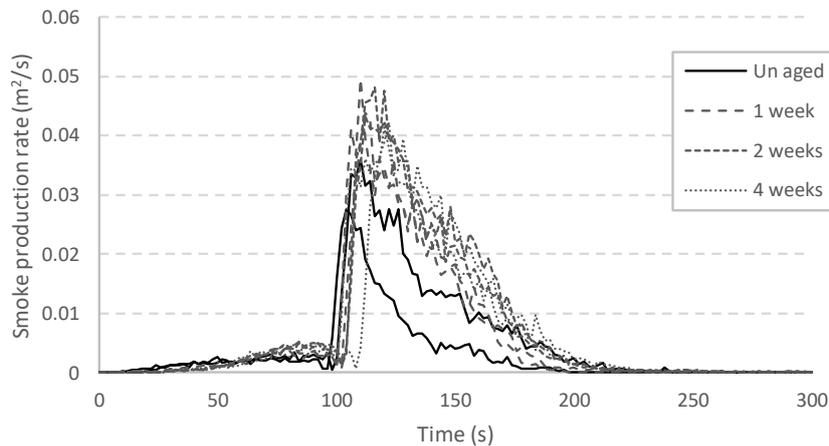


Figure 5. Smoke production rate as a function of time, moisture aged material, duplicate tests.

5. Conclusions

The test results showed that there are changes in reaction-to-fire properties when the material is aged, i.e. age matters. For the samples exposed to thermal ageing, there was a clear decrease in time to ignition, the heat release rate was increased, and the smoke production was increased. For the samples aged in moisture climate, there was a limited influence on the time to ignition, but the heat release rate and smoke production were increased compared to the unaged samples.

The main conclusion from the results is that there is a change in fire properties of the Phenolic/Basalt composite material when exposed to accelerated ageing. The results indicate that ageing deteriorates the material properties concerning fire safety. However, this study was conducted with one selected composite material only. Further testing with accelerated ageing is needed to better understand the effect of ageing on composite materials and the fire behaviour.

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