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## Accelerated Heat Aging Study of Phenolic/Basalt Fiber Reinforced Composites

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### ABSTRACT

One of the greatest impediments to use polymer-matrix composites is their susceptibility to degradation when exposed to the elevated temperatures and the limited knowledge on the thermal and mechanical properties of these composites at such temperatures. The objective of this study is to evaluate the effects of accelerated heat aging on the tensile properties of the Woven Basalt/Phenolic (WBP) composites. Mechanical tests are performed on the specimens, which have previously been subjected to the accelerated heat aging conditions. The specimens were exposed to the constant temperatures in the range of 150 °C, 200 °C and 250 °C for various periods of times, and then, the residual tensile properties were measured at room temperature. The specimens were isothermally heated for 1, 2, 5, and 10 hours at the said temperatures and then left to cool naturally to the ambient temperature of about 25 °C. Both the tensile modulus and the ultimate tensile strength of WBP composites decreased with elevated temperatures and these degradations were time and temperature dependent.

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## 1. Introduction

The Polymer Matrix Composites (PMCs) are commonly used as structural components in aerospace applications such as engine components and skins of supersonic aircraft [1]. Despite their low density and excellent mechanical properties, PMCs are known to be sensitive to the environmental factors. In particular, the elevated temperatures coupled with oxidation aging can lead to a significant reduction in mechanical properties. In order to support the advanced materials for the next-generation supersonic transport, enter and travel through the atmosphere, it is necessary that to evaluate the durability of advanced PMCs under the thermo-oxidation conditions.

In the PMCs, the thermo-oxidation mechanism strongly depends on temperature and oxygen pressure [2], specimen geometry, anisotropy [3-5] and matrix-fiber bonding [6]. It is well known that the free surfaces of high-temperature PMCs are susceptible to oxidation that leads to the development of surface and ply cracking. Once ply cracking has initiated, new free surfaces are introduced into the composite providing pathways for oxidants that inevitably lead to the degradation of the fiber matrix interfaces, reducing the lifetime and durability of these material systems [3].

Mouritz et al. subjected several types of laminate to a controlled heat flux and measured the residual properties at room temperature [7-10]. It is noticed that the high temperature can also lead to polymer post-curing [11-14]. Tsotsis and Lee [15] show that residual stresses arising from aging-induced differential resin shrinkage and interaction between plies of different orientations are found to have a strong effect on the degradation process for the plies close to the surface and, especially, near free edges. Feih et al. [16,17] indicate that the tensile failure of fiberglass composites in high temperature is dependent on the thermally induced strength reduction of both the polymer matrix and the fibers. Adams et al. [18] show the effects of space environment on the cross-ply composites and conclude that the cracks tend to avoid resin rich areas and delamination grows from transverse cracks. The phenolic resins are regarded as good engineering materials, since they are cost effective, while they have excellent temperature resistance [19]. In constructing aerospace components, the most important application of phenolic resins is in the manufacturing of high performance composites with the additional benefit of inherent flammability resistance in the structure. It is important that phenolic resins exhibit delayed ignition coupled with low heat release, low smoke evolution with little gas emission, and significant strength retention at elevated temperature. Such a material exhibits exceptional fire resistance and when incorporated into a fiber, can be used in critical applications where passenger safety in case of fire is very important. It is known that the basalt fibers have high

chemical stability [20,21]; they are non-toxic, non-combustible [22], freely withstanding temperature differences of -200 °C to +700 °C [23], can easily being processed, eco-friendly, and inexpensive [24,25]. Moreover, their specific mechanical properties are comparable with, or better than, those of E-glass ones. Utilizing cheap basalt fibers in combination with commercially available resins therefore offers a unique potential for developing inexpensive composite materials with remarkable performance at temperatures limited by the thermal stability of basalt [26].

Many researchers have studied the mechanical and thermal properties of continuous or short basalt fibers as reinforcement in the PMCs [27-30]. But, very few studies are done to evaluate the elevated temperatures influence on the mechanical properties of basalt fibers reinforced polymer composites. In this study, the effects of accelerated heat aging on the tensile properties of woven basalt fibers combined with a phenolic resin, both of which are known for high heat resistant properties at room temperature before and after accelerated heat aging is determined experimentally.

## 2. Experimental Procedures

### 2.1. Materials and Fabrication

The composite material used in this study consisted of 4 plies of woven basalt fibers (BAS 630, Basaltex™, Belgium) and a phenolic resin (Phenlam® CL2000T, Huntsman Chemical Company, Australia). The materials were fabricated in the form of plates with dimensions of 400 mm × 400 mm × 2.5 mm. The fiber volume fraction was approximately 35% in all the composite specimens. The materials were combined and the plates were fabricated by hand lay-up technique. Preliminary cure of the composite specimens was done at 60 °C for 1 h. To ensure complete curing and to achieve better properties, the composite specimens were post-cured at 80 °C for 2 h by keeping them in a vacuum oven. The physical and mechanical properties of the resin and the fiber used in this study are presented in Table 1.

### 2.2 Specimen Preparation

The specimens were cut from the plates in the desired dimensions of 250 mm × 25 mm × 2.5 mm, using a water jet cutting machine. Each specimen was polished using an emery polish paper. In this way, the local surface and edge cracks and the local surface material heterogeneities were avoided. Cutting to predetermined dimensions according to ASTM D 3039 for tensile test, the specimens were labeled and their dimensions and mass were measured. After accelerated heat aging, the woven E-glass/polyester end tabs were used on the specimens for tensile tests.

**Table 1.** The specification of the fibers and the resin

Specification	Basalt fibers [31]	Phenolic resin [32]
Weave type	Twill 1/3	...
Thickness (mm)	0.56	...
Specific surface weight (g/cm <sup>3</sup> )	630	...
Density (g/cm <sup>3</sup> )	2.70	1.2
Tensile strength (MPa)	3000	24 - 45
Tensile modulus (GPa)	89	4
Elongation at break (%)	3.185	1 - 2
Coeff. of thermal expansion (10 <sup>-6</sup> /°C)	8	20 - 31

### 2.3 Accelerated Heat Aging Process

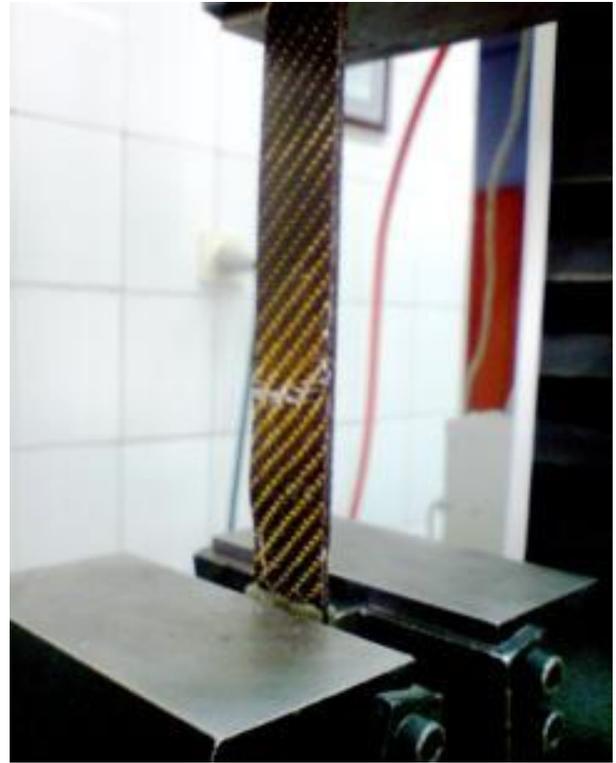
To investigate heat aging effect, the specimens were put into an air circulating oven (Model Heraeus, Germany) as shown in Fig 1. The specimens were isothermally heated for 1, 2, 5, and 10 hours at 150 °C, 200 °C and 250 °C and then left to be cooled naturally to the ambient temperature of about 25 °C.

### 2.4 Tensile Testing

Tensile tests were performed on an STM-150 20 kN universal testing machine (Santam Co., Iran) according to ASTM D3039, Fig 2. The crosshead speed was 2 mm/min and the tensile strain was measured by strain gauges attached along the specimen longitudinal axis. The tensile test was stopped when there was an obvious drop in the load-carrying capacity. The tensile tests were conducted at the ambient temperature of 25°C and the relative humidity condition of 50%. Due to the limitation of materials and testing facilities, the tensile tests properties were measured with the data taken from three specimens.



**Figure 1.** The front view of the composite specimens in the designed aluminum container inside the oven.

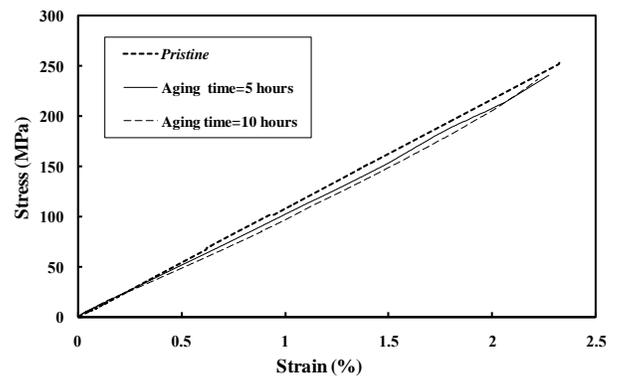


**Figure 2.** The tensile testing apparatus and the specimen.

## 3 Results and Discussion

### 3.1 Tensile Properties of Composites after Heat Accelerated Ageing

In order to obtain a clear view of the effect of heat accelerated ageing on the PMCs, the specimens made from woven basalt/phenolic (WBP) composites, are isothermally aged and the corresponding tensile responses are studied. The typical stress-strain curves for three specimens after various periods of times of accelerated heat ageing at 150 °C are presented in Fig 3. Under tension, the specimens fail in a sudden and brittle manner in general.



**Figure 3.** The tensile stress-strain of WBP composites after exposure to the accelerated heat ageing at 150 °C.

The average ultimate tensile strength and tensile modulus of the WBP composites based on the three specimens are presented in Figs 4 and 5. These data are derived from the specimens of pristine and are isothermally aged at 150 °C, 200 °C and 250 °C. The curved lines connect the averaged values.

The measurements of the ultimate tensile strength and the tensile modulus changes in WBP composite specimens show significant differences between the different aging conditions. The tensile properties of degradation are significantly higher for the heat ageing at 250 °C than 150 °C and 200 °C as shown in Figs 4 and 5.

As can be seen in Figs 4 and 5, after an initial drop in ultimate tensile strength and tensile modulus of the WBP composites during the early 5 hours in the isothermal aging at 150 °C and 200 °C, the tensile properties are relatively constant throughout the remainder of the test. Conversely, there is an obvious steep and a rapid decrease in the tensile properties of the WBP composites with increasing the elevated temperature to 250 °C isothermal aging, perennially, indicating that a steady-state condition may not have been reached. Moreover, all of the specimens aged at 250 °C show a very large scatter in the strength values.

The overall conclusion drawn here is that there are a number of mechanisms which can be held as responsible for causing degradation and stiffening of the materials during the accelerated heat ageing procedure. When the composite specimens are subjected to elevated temperatures under oxidizing atmospheres, the high temperatures probably involve a thermo-oxidation of the matrix. This phenomenon of thermo-oxidation primarily affects the external surfaces of the specimens and leads to high local stresses that can be favorable to debonding between fibers and matrix or/and to crack initiation.

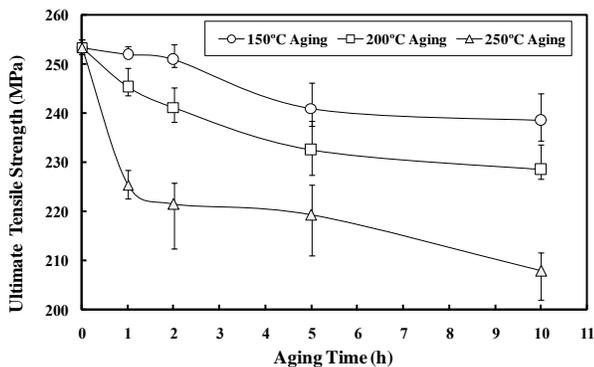


Figure 4. The ultimate tensile strength versus the accelerated heat ageing time for different aging temperature

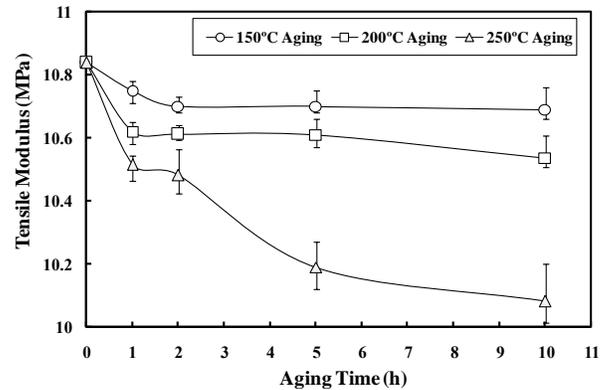
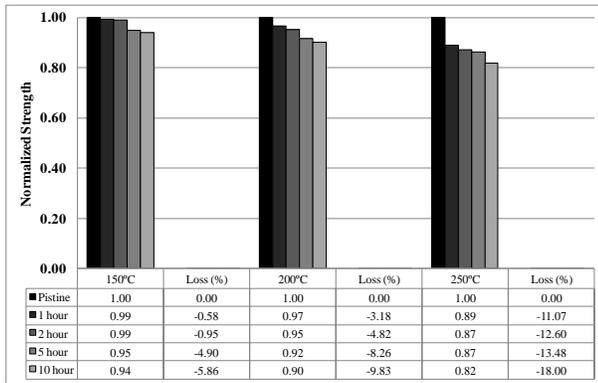


Figure 5. The tensile modulus versus the accelerated heat ageing time for different aging temperatures.

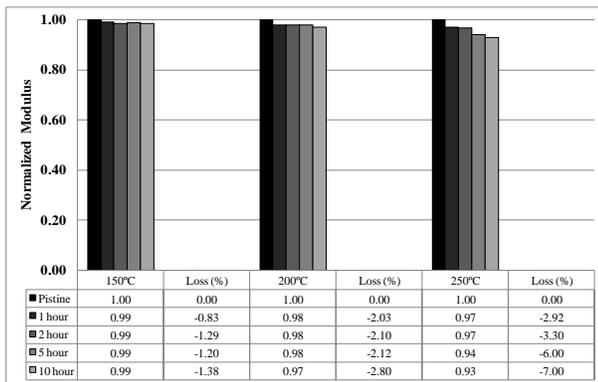
As the test duration increases, one can observe on the edges of the specimens that these short micro cracks grow through the layer thickness and develop. The number of these cracks in both internal and external layers increases with increasing aging time and consequently can lead to the degradation of the mechanical properties [24].

The most plausible explanation of the stability in tensile stiffness that occurred in the WBP composites is a possible post-curing that takes place during the accelerated heat ageing procedure at 150 °C and 200 °C after 5 hours. This happens due to a high temperature, which is not severe enough to break the more chemical bonds of the polymer [33–35], but in contrast, it contributes to the creation of free radicals to the molecules of phenolic which has not already reacted, and thus, to a further cross-linking [13,35]. These post-curing phenomena can dominate over the de-adhesion effect of thermo-oxidative ageing. Thus, the stability in the tensile properties is reflected for the WBP composites at 150 °C and 200 °C. This can help in strengthen the adhesion. But, the weakening effect of thermo-oxidative ageing might dominate over the post-curing hardening effect in the WBP composites at 250 °C and thus consequently, it may result in softening process and the steep reduction of the tensile properties.

For the sake of clarity, the values of ultimate tensile strength and tensile modulus at various temperatures are normalized to the room-temperature value of ultimate tensile strength and the tensile modulus and their ratios are plotted in the graphs (Figs 6 and 7). As a general rule, the strength and modulus of the WBP composites after exposure are lower than those of pristine specimens, and decrease with increasing the accelerated heat ageing time.



**Figure 6.** The degradation of ultimate tensile strength of composites after exposure to the accelerated heat ageing.



**Figure 7.** The degradation of tensile modulus of composites after exposure to the accelerated heat ageing.

As shown in Figs. 6 and 7, it is obvious that the WBP composites are more susceptible to damage by the accelerated heat ageing at 250 °C as compared with the accelerated heat ageing up to 200 °C. After 10 hours of exposure, the ultimate tensile strength of the WBP composites reduces by almost 6%, 10%, and 18% at 150 °C, 200 °C and 250 °C, respectively. While the tensile modulus shows a slight decrease rate with increasing the accelerated heat ageing, after 10 hours of exposure, the tensile modulus of the WBP composites reduces slightly by almost 1%, 3%, 7% at 150 °C, 200 °C and 250 °C, respectively. Furthermore, a small decrease in the failure strain of the aged WBP composites can also be observed. These changes are indicative of embrittlement in the case of the aged WBP composites.

### 3.2 Appearance of the Fracture Surfaces

Figs. 8 and 9 show the fractured specimens in the tensile after the accelerated heat ageing at 150 °C and 200 °C, respectively. The fracture surface of the WBP composites exposed to accelerated heat ageing up to 200 °C is very rough, which indicates that its failure is the result of a ductile deformation. Moreover, some kind of interfacial debonding, delamination, and fiber breakage could be seen in the WBP composites exposed to the accelerated heat ageing at 150 °C (Fig. 8). The origins of these types of failure modes are often the cracks that

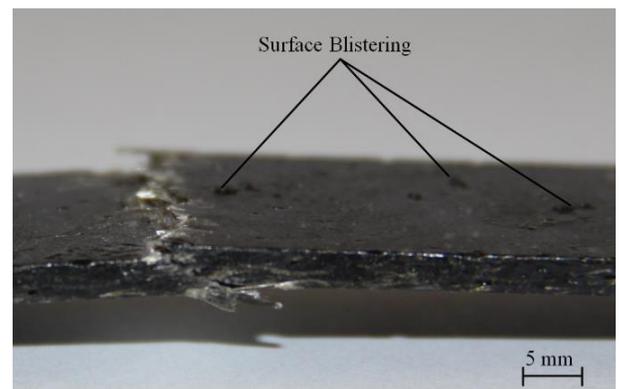
have been occurred during the heat ageing process. Delle et al. [36] have shown that due to the matrix shrinkage that occurs in accelerated heat ageing, the high strain gradients generate areas close to fibers in the matrix, which lead to these crack initiation.

The severe decrease in the tensile properties is a direct result of the removal of the matrix due to the high thermo-oxidation at the elevated temperature. The smooth fracture surface of the WBP composites exposed to accelerated heat ageing at 250 °C suggests that it has a brittle failure mode (Fig. 10).

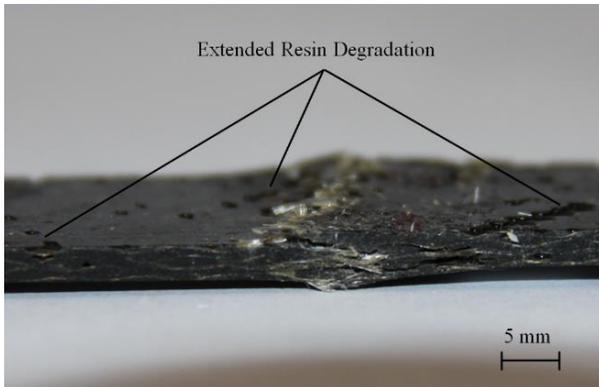
As the outer layers of the resin degrade, the fibers are no longer able to carry load or at least are less able to carry load than without any resin degradation. This reduces the strength by reducing the number of load-carrying fibers. The accelerated heat ageing does degrade an outer layer of the material as well as causing microcracks. Although the outer-layer degradation may be somewhat uniform (because the medium through which the air (oxygen) diffuses is largely uniform along the length of the specimens), the formation of the microcracks is likely to be dependent on the local defects and stochastic processes. The increased scatter in the data at longer exposure times suggests that the potential for large strength degradation increases significantly with increasing the heat ageing temperature. The removal of the matrix at the surface of composite specimens and some blisters can be seen in Fig. 10.



**Figure 8.** The fractured specimen of WBP composite exposed to the accelerated heat ageing at 150 °C after the tensile test.



**Figure 9.** The fractured specimen of WBP composite exposed to the accelerated heat ageing at 200 °C after the tensile test.



**Figure 10.** The fractured specimen of WBP composite exposed to the accelerated heat ageing at 250 °C after the tensile test.

## 5. Conclusions

In this paper, the accelerated heat ageing of basalt/phenolic composites is investigated by characterizing the reduction in tensile properties at 150, 200 and 250 °C. In conclusion, the basalt/phenolic composites are a durable and stiff polymer matrix composite that are capable of withstanding extreme thermal aging up to 150 °C. This material showed the relative stability at 200°C after the approximately 5 hours heat aging. After 10 hours, the composites suffered 6, 10, and 18% tensile strength reduction as well as 1, 3 and 7% reduction in tensile modulus at 150, 200 and 250 °C, respectively.

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