EFFECT OF ACCELERATED AGING ON CARBON FIBER / EPOXY COMPOSITES AND NEAT EPOXY RESIN

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ABSTRACT

The use of carbon fiber / epoxy composites is steadily increasing due to the improved properties of the material and high quality of the finished part. These materials are especially attractive to aeronautic and aerospace industries due to the combination of material properties required for those applications and the importance of weight reduction in such structures. The influence of operational environments on the long-term durability of structural components fabricated with advanced polymer-matrix composite materials is an ongoing concern. Thus, investigating the aging process of the neat polymer matrix is very important in order to understand the effects of aging on polymer composite materials, as well as at the interface between fiber and polymeric matrix. In this work, carbon-epoxy composites and neat epoxy specimens were subjected to accelerated aging in an aging chamber with controlled conditions of temperature, humidity and UV-radiation. The effects of aging were evaluated by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Fourier-Transform Infrared (FTIR) Spectroscopy. Mass change of the specimens due to aging was monitored by weighing specimens before and after the accelerated aging process. Composite samples were also investigated by Scanning Electron Microscopy (SEM).

1 INTRODUCTION

As the use of polymer matrix composite (PMC) materials in aeronautic structures is steadily increasing, the influence of environmental service conditions on the durability of these materials is an ongoing concern for the aeronautic industry and airline companies. Such structures should be designed to withstand operational conditions imposed throughout the service life. The influence of environmental factors such as moisture, temperature and UV radiation on the durability of PMC aeronautic structures should be better understood and considered during structural design.

The lack of resistance of polymer composite structures to degradation agents often becomes apparent within a short period [1]. In some circumstances, only a few hours of exposure may lead to catastrophic failure or seriously compromise structural integrity. Irreversible property changes in PMCs can be induced by degradation agents acting individually or collectively, including elevated temperatures, humidity and UV-radiation [1].

The consequences of moisture absorption by the polymeric matrix include plastification, reduction of the glass transition temperature, increase in creep and stress relaxation, decrease in mechanical strength and elastic modulus [2, 3, 4, 5, 6, 7]. The absorbed moisture may also react with unreacted groups of the epoxy structure, influencing therefore the aging process [8].

UV-radiation may induce degradation of the polymeric surface of the composite, ultimately exposing the fibers and affecting mechanical properties, in addition to increasing moisture absorption [9,10]. When a polymer is exposed to solar radiation, the energy absorbed results in the formation of free radicals, with further reactions leading to the formation of hydroperoxides, which can then dissociate to produce a series of decomposition products including aldehydes and ketones. The presence of carbonyl groups in a degraded polymer can be used as a chemical index for degradation

[1]. Oxidation of the polymer increases chain stiffness and causes embrittlement of the material surface. Literature reports show the formation of carbonyl groups in aged epoxy material [5, 11].

Moisture absorption and UV degradation may produce significant effects on mechanical properties of composite materials, affecting the reliability of these materials for long-term use in structural applications. Although the deleterious effects of aging are known, the mechanisms of interaction of the degradation agents with the exposed composite material and their contribution to the degradation process are still a matter of intense study. In order to better understand the effects of aging on the composite material, neat polymeric resins must be investigated. The polymeric matrix is known to be the most affected part of carbon fiber reinforced composite materials, as carbon fibers are stable in most environments. Thus, understanding how aging affects the polymeric matrix of the composite may be the starting point to understand the degradation of properties of the composite material as a whole, including the fiber-matrix interface. The correlation of chemical and physical changes within the polymeric matrix may then be correlated to the degradation of properties observed for the composite material.

In this study, carbon-epoxy composites and neat epoxy specimens were subjected to accelerated aging in an aging chamber with controlled conditions of temperature, humidity and UV-radiation. Changes on the epoxy matrix and composites are evaluated by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Fourier-Transform Infrared (FTIR) Spectroscopy. Composite samples were also investigated using Scanning Electron Microscopy (SEM).

2 EXPERIMENTAL

Carbon-epoxy composites and neat epoxy resin were evaluated in this study. Composite samples with dimensions 2.13 mm x 9.87 mm x 19.90 mm (thickness x width x length) – Group 1 - and samples with dimensions 1.10 mm x 15.15 mm x 79.91 mm (thickness x width x length) – Group 2 - were used. Neat epoxy resin samples were cut with dimensions of approximately 6 mm x 10 mm x 20 mm (thickness x width x length).

2.1 Accelerated aging

Composite samples were aged in an accelerated aging chamber Equilam - (Figure 1) by using UV radiation (UVA-340) and water condensation. All samples were submitted to alternated cycles of UVA radiation (8 hours) at 80ºC at 0.89 W/m²/nm and water condensation (4 hours) at 50ºC for the period of 3 months (2160 hours). Tests were conducted according to ASTM G 154 – 00a (Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials). The accelerated aging process was initiated with the moisture step and concluded after 2160 hours with the UV-radiation step.

Neat epoxy resin samples were submitted to the same accelerated aging program as the composite samples, except for the aging period, which was of 2 months (1464 hours).

Figure 1: Aging chamber used for accelerated aging studies.

2.2 Mass Change

In order to monitor mass variation of the samples, these were weighed before and after the accelerated aging procedure. The results presented for the composite material are average values of 10 samples of Group 1 and 10 samples of Group 2. For the neat epoxy resin, results correspond to the measurement of only one sample. Mass variation was calculated by using the following equation:

$$M(\%) = \frac{Final\ mass\ (g) - Initial\ mass\ (g)}{Initial\ mass\ (g)} * 100 \qquad (1)$$

2.2 Scanning Electron Microscopy (SEM)

Material morphology was analyzed using a scanning electron microscope Hitachi Tabletop Microscope TM-3000. Before the accelerated aging, the cross-sectional area of Group 1 samples was polished using silicon carbide grinding paper (400 to 2000 mesh) and then polished with alumina suspension of 1.0 µm. This procedure was carried out to allow visualization of the carbon fibers at the cross-section of the samples, so that the effect of aging on sample morphology could be better assessed.

Care was taken to obtain SEM images of the same specimen at the same spot, before and after the aging process. This procedure allowed a direct comparison of the same surface, so that the effects of accelerated aging could be assessed.

Only composite samples were investigated by SEM; neat resin samples were not.

2.3 Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier-Transform Infrared (FTIR) Spectroscopy of Group 1 samples was performed using a Shimadzu IRAffinity spectrophotometer, in order to compare the spectra of unaged and aged material. The analysis parameters were 32 scans, 700 - 4000 cm^{-1} range and 4 cm^{-1} resolution. Before the analysis, samples were conditioned in a desiccator. One specimen for each condition (aged and unaged) was analyzed, for both composite and neat epoxy resin material.

2.4 Thermal analysis

Both composite and neat resin samples were analyzed by Differential Scanning Calorimetry (DSC) / Thermal Gravimetric Analysis (TGA). Thermal analysis was performed using a Netzsch STA 449 F3

Jupter, following recommendations of ASTM E1131 – Standard Test Method for Compositional Analysis by Thermogravimetry. Samples with mass of approximately 20 mg were used. The heating rate was 10 K/min, from room temperature to 600 °C. Inert gas (N_2) at 50 mL/min was used. The same test was performed simultaneously for TGA and DSC.

3 RESULTS AND DISCUSSION

3.1 Mass Change

Mass loss caused by accelerated aging is shown in Table 1:

Sample type		Mass variation	Std. Dev.
Group 1	[%]	-0.58	0.08
Group 2	[%]	-1.08	0.05
Neat epoxy	[%]	-2.39	-

Table 1: Mass loss caused by accelerated aging.

All samples showed mass loss caused by accelerated aging. According to the results presented in Table 1, the mass loss of composite specimens of Group 2 was greater than for those of Group 1. This difference can be explained by the difference in exposed area of material with respect to sample volume. In specimens of Group 1, the exposed area was reduced due to the presence of tabs.

The mass loss of the neat epoxy specimens was greater than for the composite samples. The result indicates that material degradation is more pronounced in samples that lack fibers due to two main reasons: 1) the mass loss occurs in the matrix and the matrix volume fraction is about 50% on the composite specimens; 2) the presence of fibers in the composite samples offers partial protection to the polymeric matrix against UV-radiation during accelerated aging.

3.1 Scanning Electron Microscope (SEM)

The SEM images in Figure 2 show the laminate layers and carbon fiber / polymer matrix distribution along the cross-sectional area. Figure 2 (a) shows the surface area of a cross-section of the unaged specimen. Layers are well-compacted and there is an uniform distribution of the carbon fibers along the epoxy matrix. For specimens subjected to accelerated aging (Figure 2 (b)), matrix loss and degradation of the material at the fiber / matrix interface with exposure of carbon fibers are evident.
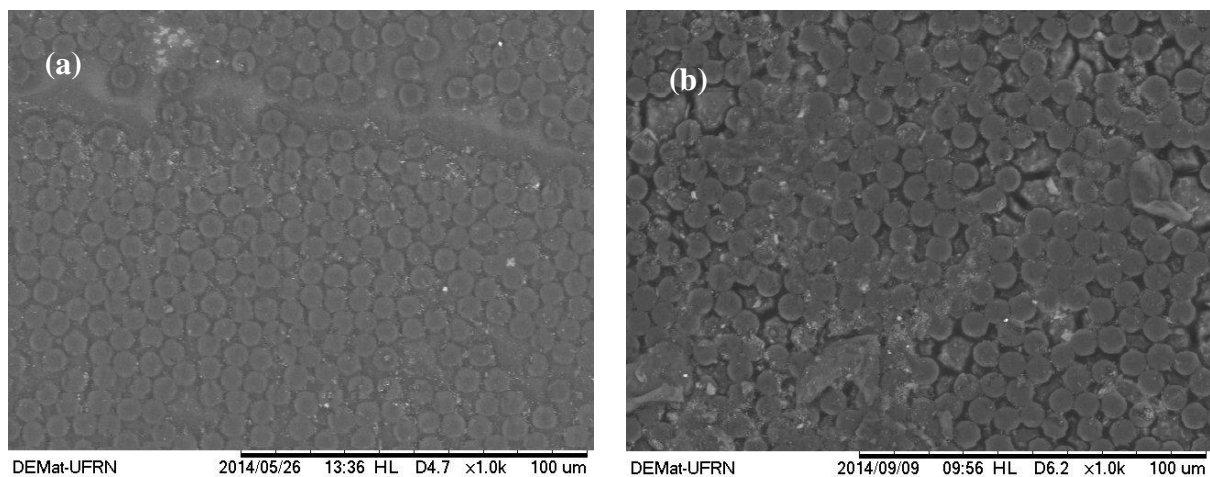

Figure 2: Typical specimen cross-sectional area. (a) unaged (b) aged.

3.2 FTIR Spectroscopy

Figure 3 shows FTIR spectra for aged and unaged specimens. Results suggest that the material is changed during accelerated aging. The reduction in intensity of the –OH peak (3304 cm-1) and the increased intensity of the carbonyl peak (1647 cm-1) were the most significant spectral changes, which indicate chemical alterations related to the degradation of the epoxy resin in the composite.
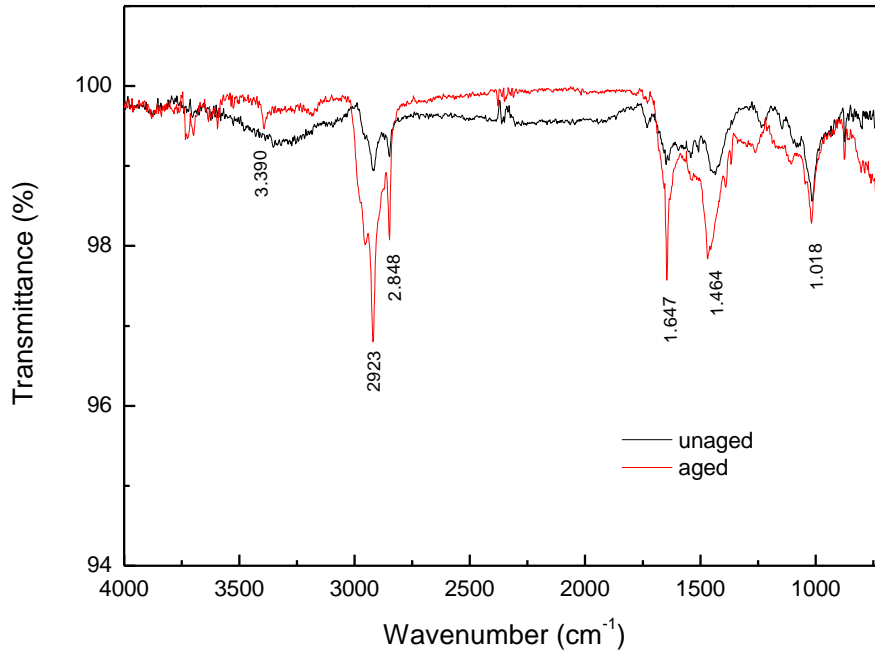

Figure 3: FTIR spectra for aged and unaged composite samples.

Results obtained for neat epoxy samples (Figure 4) show that the chemical changes were less pronounced than the changes observed for the composite samples. No indication of formation of carbonyl groups was detected. One possible reason for not detecting chemical changes within the neat epoxy resin is that resin samples were submitted to a shorter accelerated aging time as compared to composite samples. Further tests with longer aging periods are being carried out and further studies regarding chemical changes of the materials are being conducted.
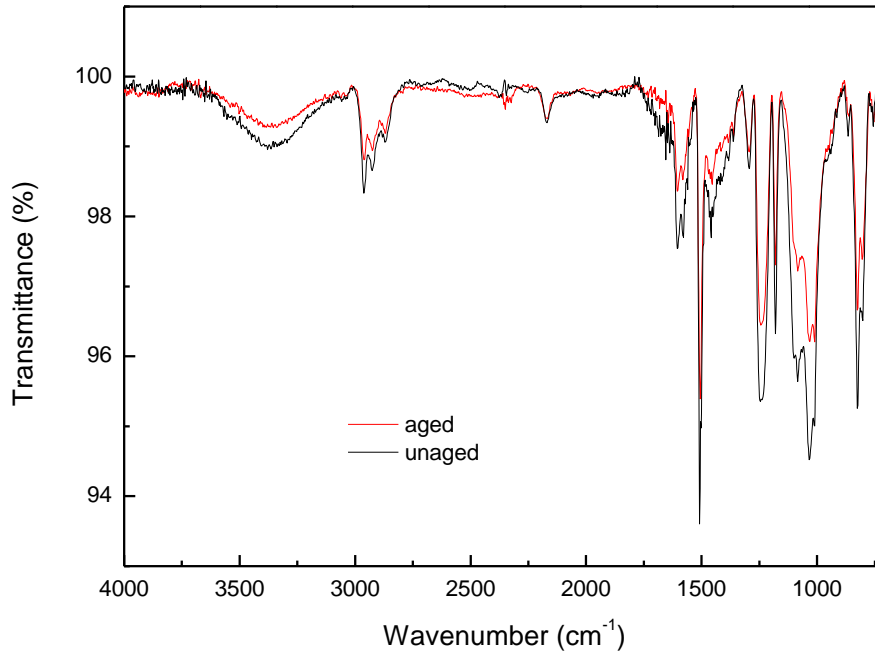
Figure 4: FTIR spectra for aged and unaged neat epoxy samples.

3.2 Thermal analysis

TGA results obtained for aged and unaged composite samples are shown in Figure 5 (a) and DSC results are shown in Figure 5 (b).

TGA and DSC results show no significant changes on mass loss, rate of mass loss or heat flow between aged and unaged material. Although samples were taken from the surface directly exposed to UV-radiation during accelerated aging, it seems that the fiber volume fraction was too high for detecting possible changes within the material.
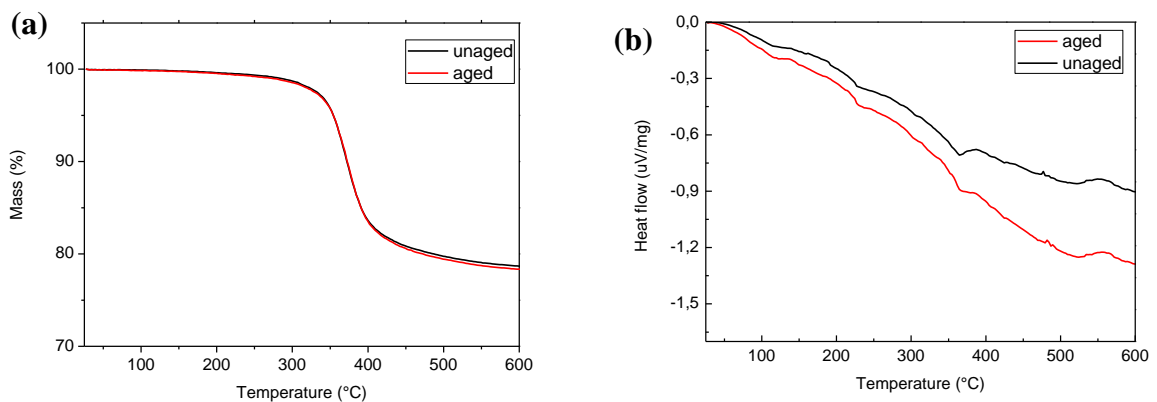

Figure 5: Curves for aged and unaged composite samples. (a) TGA curves (b) DSC curves.

TGA results obtained for aged and unaged neat epoxy samples are shown in Figure 6. Tg values obtained for aged and unaged material are 238.3°C and 242.9°C, respectively. The slight decrease in Tg caused by aging may be related to residual water within the sample, which may have plasticized
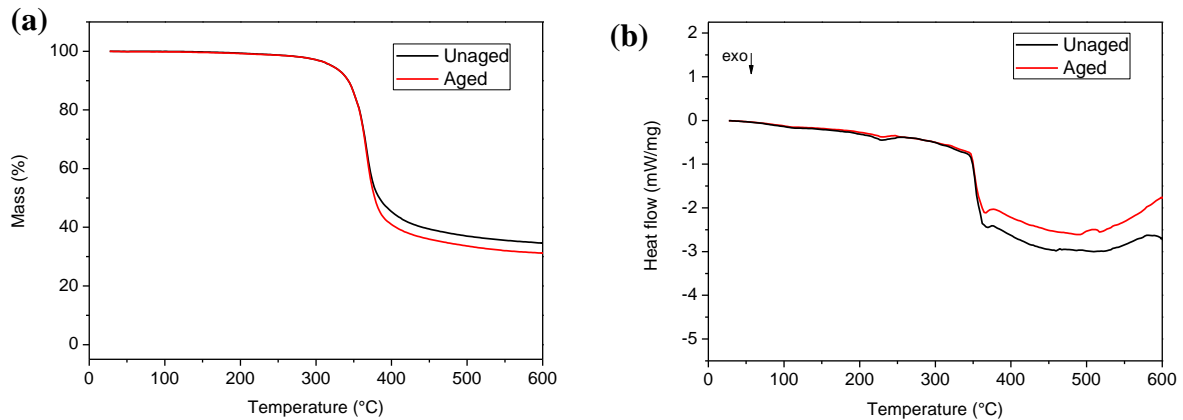
the epoxy material.

(a)

(b)

Figure 6: Curves for aged and unaged neat epoxy samples. (a) TGA curves (b) DSC curves.

4   CONCLUSIONS

In this study, the effects of accelerated aging on carbon-epoxy composites and neat epoxy were investigated. Samples were submitted to aging in an accelerated aging chamber using UV-A radiation and water condensation in alternating cycles. Composite samples and neat epoxy samples were aged for 3 months and 2 months, respectively. Accelerated aging caused mass loss in all materials investigated. The mass loss was greater in neat epoxy specimens than those of composite material for two reasons: the mass loss occurs in the matrix and the matrix volume fraction is about 50% in composite specimens; the presence of fibers in the composite samples offers partial protection to the polymeric matrix against UV-radiation during accelerated aging. SEM images of samples subjected to accelerated aging indicate that matrix loss and degradation of the material at the fiber / matrix interface with exposure of carbon fibers are evident. FTIR-spectra show chemical changes within the composite material due to accelerated aging. Chemical changes were less pronounced on the neat epoxy due to the shorter accelerated aging time to which this material was subjected, as compared to the composite samples. TGA and DSC results show no significant changes between aged and unaged material, except for a slight decrease in Tg on aged specimens, which was attributed to residual water within the sample, which may have plasticized the material. Despite the short accelerated aging time period, results show that aging causes chemical and morphological changes in the polymer composite material studied. Further tests are being conducted for longer aging periods and further studies regarding chemical changes of the materials are being developed.

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