DURABILITY OF COMPOSITE MATERIALS IN DEPLOYABLE STRUCTURES FOR SPACE APPLICATIONS

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Abstract
Advanced composite materials are an excellent option for flexible deployable space structures, such as deployable antennas and booms. However, the harsh environment in space can degrade the performance of composite materials, thus limiting their wider application. In low Earth orbit (LEO), atomic oxygen (AO) resistance is a key limitation to service longevity. In this work, the AO resistance is examined for three commercial composite materials, which undergo exposure in a ground-based facility which simulates the AO environment of space. The degradation of the performance of the materials is determined by measuring selected properties (e.g. surface chemistry, and flexural stiffness) before and after exposure. The results indicated that the resin on the surface of all laminates has almost been entirely eroded and suffered significant degradation after exposure. The results presented in this work can act as a benchmark for the development of new composite systems or protection technologies which can provide an extended service life for flexible deployable structures in LEO.

1. Introduction

Polymer-based fibre-reinforced composites have unique properties such as low weight and outstanding mechanical properties [1]. These advantages make composite materials promising candidates in space applications such as deployable structures and spacecraft components. However, the durability of composite materials is limited in the harsh environment in space, which includes high vacuum, vacuum ultraviolet (VUV) radiation, extreme thermal cycling, and the risk of atomic oxygen (AO) erosion [2]. AO erosion plays a leading role in the degradation of polymer based composite materials, especially in low Earth Orbit (LEO) [3]. When the surface of polymer based composites is attacked by AO, the high energy can break the chemical bonds of the composite, which degrades the properties of the material [4]. This surface degradation is particularly detrimental for deployable structures which rely on material compliance for compact stowage during launch, by bending and folding ultra-thin composite laminates [5]. The high deployment strains limit application of protective coatings, and other methods for AO protection must therefore be sought.

To understand the AO resistance of various material, several in orbit tests have been performed by various institutes, such as such as European Space Agency (ESA) flight experiment [6], Space Environment Exposure Device (SEED) projects by JAXA [7], Evaluation of Oxygen Interaction with Materials (EOIM)-3 by JAXA and NASA [8], and MISSE by NASA [9]. A large amount of research has been undertaken to investigate the AO resistance of composites materials using ground-based facilities, but few publications focus on the AO behaviour of space-qualified composites which are already used in orbit. In this paper, the AO resistance of three selected composite materials were examined to assess their longevity, in order to act as a benchmark for the development of new matrix materials later in the programme.

2. Experimental Methods

2.1. Materials

Two resin systems which are commonly used for commercial applications are used in this work(supplied by Solvay), they are well characterized by their high glass transition temperature (T_g), thermal stability and high modulus. The structure, along with the designations used, are shown in Table 1.

**Table 1.** Materials used in this work.

Material	Laminate description	Lay-up (woven fabric)
LAM 01	Carbon fibre reinforced epoxy resin A	(±45/0/±45) [‡]
LAM 02	Carbon fibre reinforced epoxy resin B	(0/90)₃
LAM 03	Carbon fibre/Kevlar reinforced epoxy resin B	(±45/0/90/±45) [*]

* Kevlar in the middle ply and carbon fibre on top and bottom ply

‡ The middle ply is UD

The chemical structures of these materials are shown in Figure 1. LAM 01 uses a resin system which contains (a) traglycidyl-4,4'-diaminodiphenylmethane (TGDDM) cured by (c) diaminodiphenylsulfone (DDS). LAM 02 and LAM 03 use the same resin system which is formulated from a blend of two epoxy resins: (a)TGDDM and (b) bisphenol A diglycidyl ether (DGEBA), cured with (d) dicyandiamide (DICY).
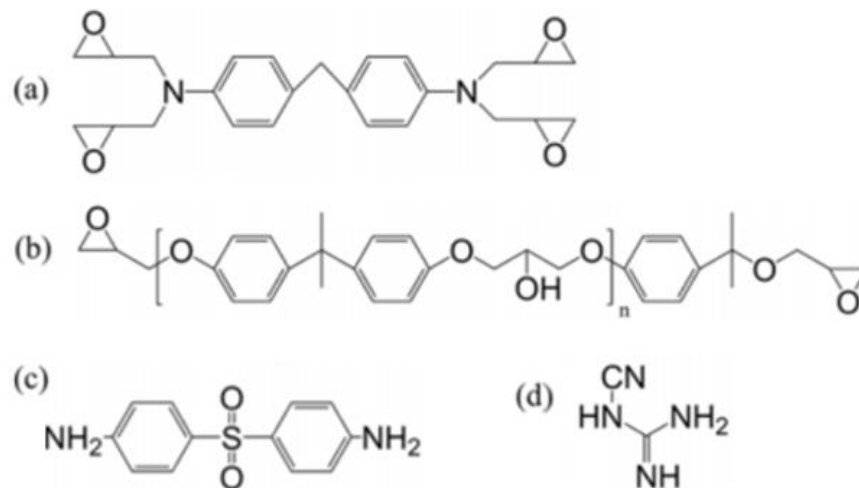
Figure 1. Chemical structures of epoxy resin A: (a) TGDDM cured with (c) DDS and epoxy resin B: (a) TGDDM and (b) DGEBA blend cured with (d) DICY [10].

2.2 Exposure Test

The atomic oxygen (AO) exposure test was carried out using a radio-frequency (RF) plasma asher. Plasma was generated in a glass tube (length 300 mm, diameter 105 mm) and the samples were placed within, on an aluminium panel. The pressure in the main chamber was 1.0 mbar while gaseous oxygen was pumped into the chamber at around 0.2 NL/min. AO fluence was calculated based on the mass loss of a reference Kapton™ polyimide sample, with a well characterized erosion yield (3.0×10^{24} cm³/atom) in the LEO environment [11]. The laminates were exposed in three successive cycles, and their mechanical, chemical, and surface properties were assessed after each cycle.

2.3 Three-Point Bend Test

The flexural stiffness of thin laminates is expected to be particularly sensitive to surface erosion due to atomic oxygen, and was therefore selected to characterise their mechanical properties. The test protocol consists of applying a three-point bend test in the elastic region, subsequently exposing the sample to

Yanjun He, Agnieszka Suliga, Alex Brinkmeyer, Mark Schenk and Ian Hamerton

atomic oxygen, and finally performing the three-point bend test again to assess the change in flexural properties.

The test was conducted on Shimazu Mechanical Test Machine with a maximum load of 1 kN, following procedure A of the ASTM D790-15 standard [12]. The laminates were cut into test specimens (38×14 mm). The ASTM standard recommends a span to thickness ratio of 16:1. However, Zweben *et al.* [13] reported that for thin samples, the span to thickness ratio should be more than 60:1 to obtain an accurate result. Thus, the span used in this test was 22 mm.

The main output of this tests is the flexural modulus, which is calculated by the following Eq.1 [13]

$$E=PL^3/4bt^3\delta. \tag{1}$$

where E is the flexural modulus (GPa), L is the support span (m), δ is the deflection of the centreline of the specimen at the middle of the support span (m), b is the width of specimen tested (m), and t is the thickness of beam tested (m). However, to avoid the effect of inconsistent thickness measurements, flexural rigidity was used to characterize the flexural properties of each laminate. Flexural rigidity governs the deflection under lateral load, which can also reflect the flexural properties of each laminate and can be calculated by Eq.2 [13]

$$Et^3=PL^3/4b\delta. \tag{2}$$

where Et^3 is the flexural rigidity (N*m).

2.4 Surface Spectroscopy

Surface spectroscopy was performed under ambient conditions before and after exposure to AO using a Perkin–Elmer Series 2000 Fourier transform infrared (FT-IR) spectrometer with a diamond Attenuated total reflectance accessory. The purpose of this test is to investigate the surface chemistry change of laminates after AO exposure.

2.5 Surface Morphology

Surface morphology was investigated using a Hitachi TM3030Plus tabletop Microscope (accelerating voltage 15 kV). This test aim at examining the surface morphology change after exposure.

3. Results and Discussion

3.1 Surface Morphology
The total AO fluence received in each exposure run is shown in Table 2, while SEM images of the three laminates before and after exposure are shown in Figure 2.

Table 2. AO fluence for each exposure.

Exposure Cycle	Exposure duration (hr)	Total AO fluence ($\times 10^{20}$ atom/cm^2)	Equivalent duration in orbit (days)[‡]
1		1.75	20
2	3	2.82	31
3		3.82	43

‡ Based on the data from the International Space Station [10]

Before AO exposure, no obvious defects were detected on the surface of three laminates (Figure 2 (a), (c), and (e)). After the third exposure, when all samples had received the highest total AO fluence, the

Yanjun He, Agnieszka Suliga, Alex Brinkmeyer, Mark Schenk and Ian Hamerton

surface resin had been severely eroded from all the laminates, exposing the fibres underneath to the AO (Figure 2 (b), (d), and (f)). Several erosion holes can be observed on the residual resin which is located in the gaps and at the edges between the warp and weft of the carbon fibre yarns in each laminate. These holes indicate that the erosion due to AO is not even, and it occurs at weaker points in the resin (*e.g.* at structural moieties which are more susceptible to attack such as hydrogen atoms bonded to alkyl fragments) and provides a path for AO to erode the underlying resin still further.
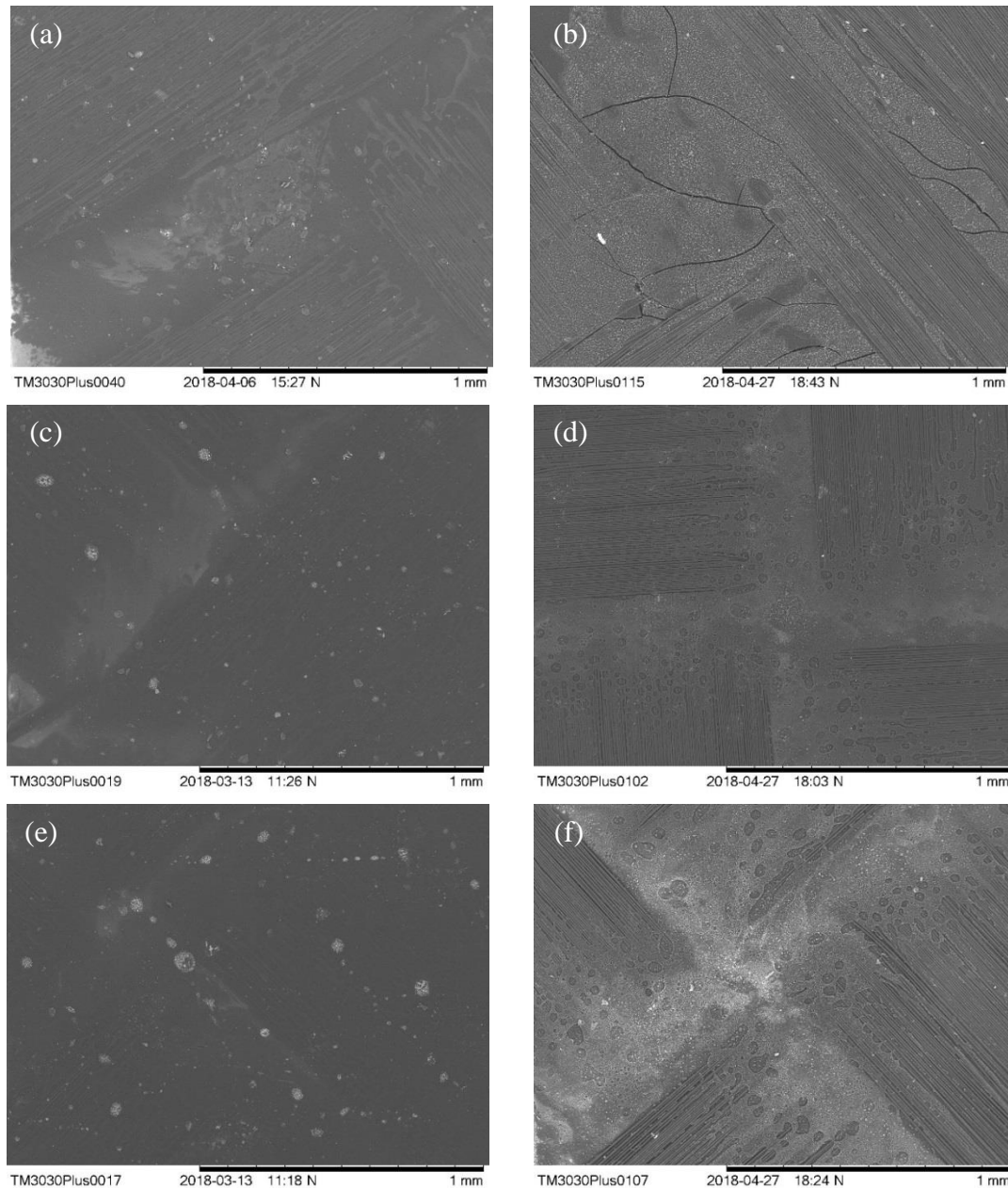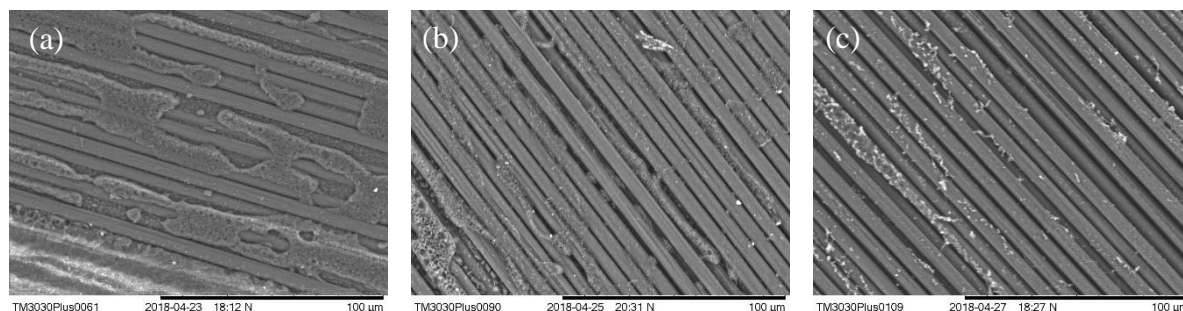

Figure 2. The surface morphologies of the LAM 01 (a, b), LAM 02 (c, d) and LAM 03 (e, f) before and after third exposure (a, c, e, AO fluence = 0; b, d, f, AO fluence = 3.82×10^{20} atom/cm^2).

In addition to the resin erosion, it is also noticeable that the resin in the gaps between the fabric yarn in LAM 01 displays significant cracks after AO exposure (Figure 2 (b)), which are not present in either LAM 02 or LAM 03. The cause of this cracking is not yet known and requires further analysis.

Figure 3 shows a gradual erosion of the surface resin for LAM 03. After the first exposure, resin was significantly eroded, and part of the underneath carbon fibres are exposed with the erosion of resin. The

resin was further eroded in the second exposure, while in the third exposure the surface resin had been almost completely eroded.

Figure 3. The surface morphology change of the LAM 03 after (a) first exposure, (b) second exposure, and (c) third exposure.

3.2 FTIR Spectroscopy

The reaction between the polymer matrices and AO is complex and depends on the chemical structures. In our work, the principal reaction with AO is believed to be through a biphenyl segment containing a saturated alkyl bridge within the chemical structure of the epoxy. The reactions take place between the polymer and two kinds of AO: the ground state (3P) and electronically-excited (1D)[14]. The ground state O (3P) can abstract a hydrogen atom in the polymer structure to form a hydroxyl group with a reaction barrier of 28.9, 18.8, and 13.8 kJ/mol. (where the abstracted H is primary, secondary, and tertiary, respectively)[14]. The O (1D) can also react with the polymer by abstracting a hydrogen atom, but it is more likely to undergo insertion into the C-H bond of a polymer with no barrier. A summary of the possible reactions is shown in Figure 4. During the reaction, volatile fragments, such as short-chain oxidation products, may leave the surface and thus degrade the performance of the materials.
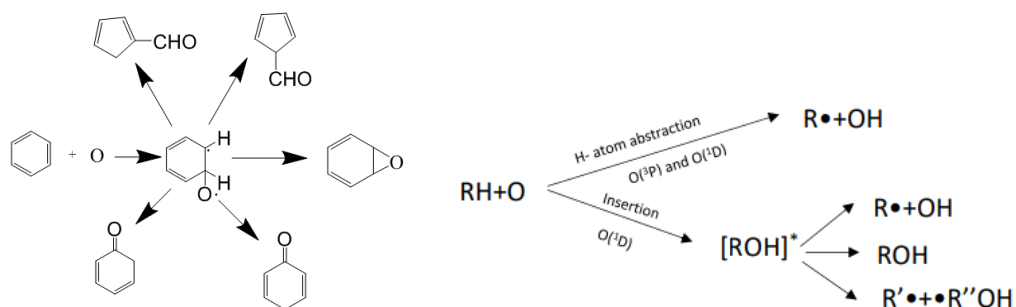
Figure 4. The mechanism of the reaction between the polymer matrix and AO[14,15]

The results of FTIR spectral analysis of LAM 03 as it undergoes exposure to the AO flux are shown in Figure 5 as a representative example. A gradual decrease in the intensity of the spectral bands can be observed in all the laminates with the increase of AO fluence. A common change within the three laminates after exposure is that the centre of the hydroxyl stretching vibration at around 3400 cm^{-1} shifts to lower frequency (3250 cm^{-1}), suggesting the loss of free O-H stretch and finally vanishes due to the reaction between AO and hydroxyl. The decrease in the intensity of the other bands also indicate the loss of the matrix from the surface of the laminates: after the first exposure, a slight reduction of intensity can be detected, which indicates that a significant amount of resin remains on the surface. However, after the second and third exposures, the intensity of the bands decreases rapidly, with only several bands (due primarily to the carbon fibres) detected after the third exposure, which is consistent with the SEM data.

Yanjun He, Agnieszka Suliga, Alex Brinkmeyer, Mark Schenk and Ian Hamerton
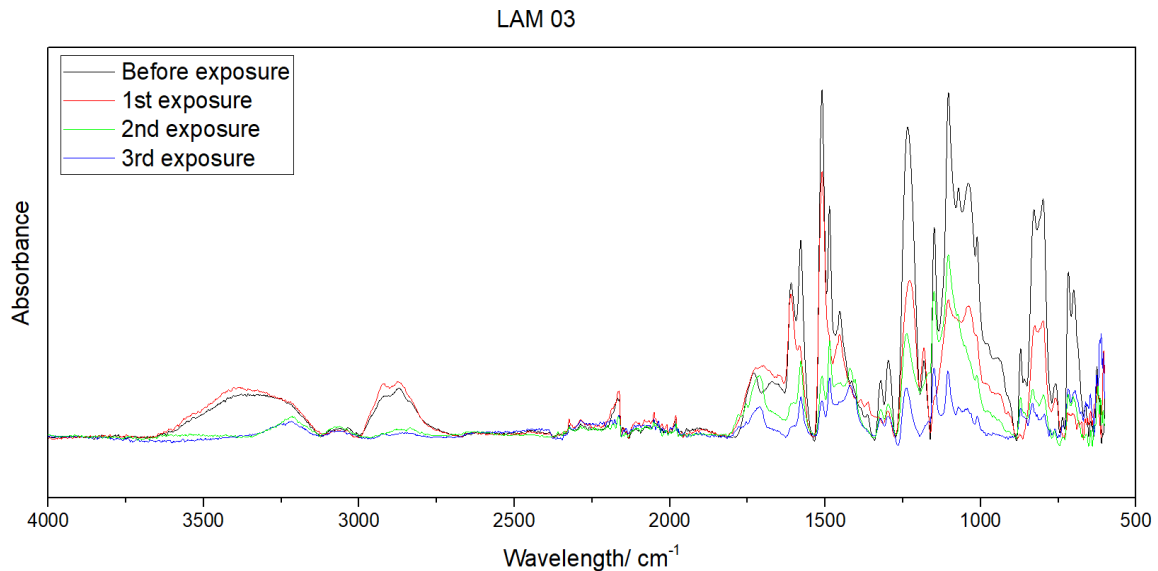
**Figure 5.** FTIR spectra of LAM 03 as a function of AO fluence exposure.

3.3 Three-Point Bend

Table. 3 shows the dimension of samples been tested and the results of the 3-point bending measurements for each laminate under different AO fluence are shown in Figure 6. There is a reduction of 5-10% in both the flexural rigidity and modulus of all laminates after the first exposure due to the erosion of resin, and a general downward trend thereafter. The SEM results in the previous section suggest that a significant amount of surface resin has been removed, exposing fibres after the first cycle. According to the in-orbit data from MISSE [10], the erosion yield of epoxy is about 10 times greater than that recorded for pyrolytic graphite (a model for the carbon fibres). Thus, after the majority of the resin has been eroded, the exposed carbon fibre is relatively resistant to erosion, although not entirely inert. Therefore, after the first exposure, the flexural properties will not change significantly unless the fibres become seriously eroded and damaged, which requires a high AO fluence.

Table 3. Dimension of all samples been tested.

Sample No		Width(mm)	Length(mm)	Thickness(mm)
	1	13.80	38.38	0.25
LAM 01	2	13.43	38.62	0.24
	3	13.85	38.20	0.25
	1	13.20	36.74	0.32
LAM 02	2	13.17	37.47	0.34
	3	13.13	37.25	0.33
	1	13.75	38.47	0.40
LAM 03	2	13.64	37.80	0.38
	3	13.95	38.91	0.39

LAM 01 displays an increase in the flexural modulus after the third exposure, which is consistent with the work of Paillous *et al.* [16], who reported that at the beginning of exposure, the erosion of the outer surface of resin results in a slight increase in fibre content, while the work of NASA's Long Duration Exposure Facility (LDEF) [17] has also demonstrated that flexural properties are sensitive to surface degradation. In the present work, the fibre content and surface conditions are likely more important variables than the graphite fibre type or epoxy matrix type in determining the susceptibility of carbon fibre reinforced epoxy composites to AO erosion. However, this does not explain why LAM 02 and LAM 03 did not experience an increase in flexural properties after exposure under the same conditions. In addition, the flexural rigidity of LAM 01 also increased after exposure, further study is needed to account for this.

Yanjun He, Agnieszka Suliga, Alex Brinkmeyer, Mark Schenk and Ian Hamerton
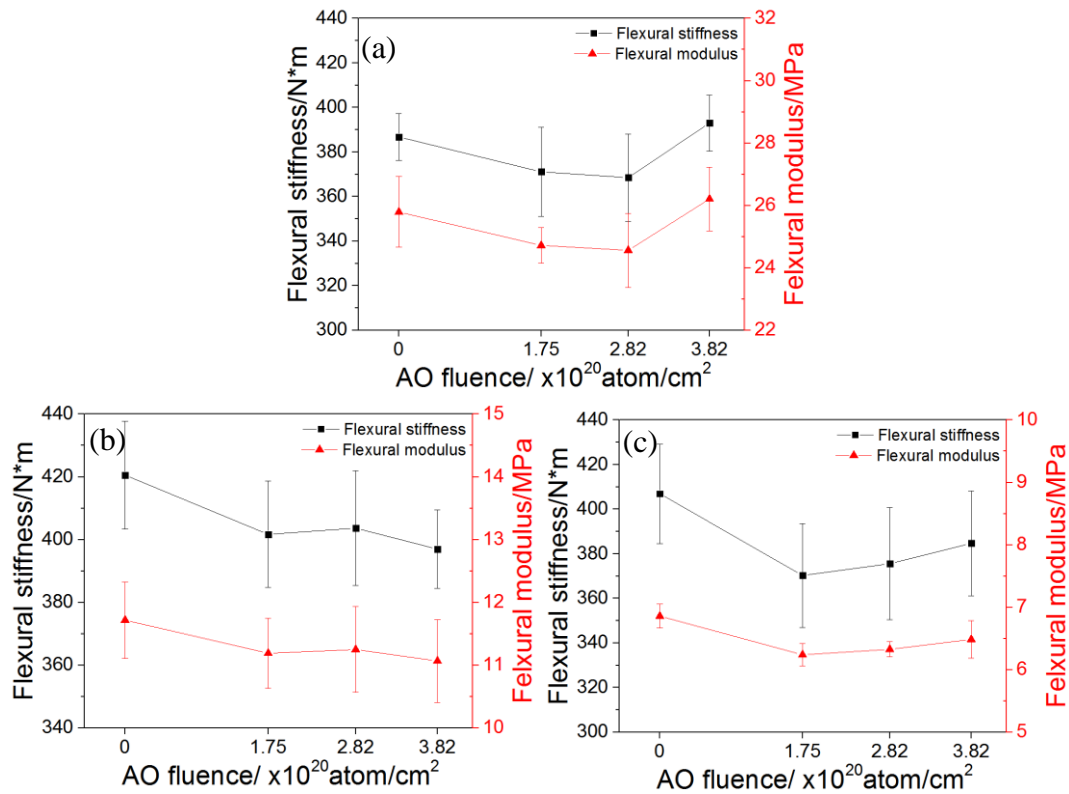
Figure 6. Flexural properties of (a) LAM 01, (b) LAM 02, and (c) LAM 03 as a function of AO fluence exposure.

4. Conclusions

In this study, the AO behaviour of three laminates have been compared. The key findings of this work are as follows:

(1) The SEM images indicate that the resin on the surface of three laminates has been almost entirely eroded after AO exposure. Some residual resin remains in the gaps and at the edges of the carbon fibre yarn. The laminates experienced a gradual erosion of surface resin with the increase of AO fluence.

(2) The results of FTIR spectral analysis suggest that the surface resin on all laminates has suffered significant degradation after exposure. After the third exposure, the spectra are principally due to the carbon fibres, with only a weak characteristic peak for the resin was observed in all laminates.

(3) The mechanical tests suggest that the flexural properties of all laminates degrade significantly after the first exposure due to the erosion of matrix. LAM 02 and LAM 03 show a slight variation in their flexural properties after the second and third exposures. The flexural properties of LAM 01 show an unexpected increase after the third exposure, and further study is needed to understand this mechanism.

Acknowledgments

Yanjun He, Agnieszka Suliga, Alex Brinkmeyer, Mark Schenk and Ian Hamerton

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