

Microstructural Changes in Carbonized Wood-Lignin, a Potential Space Material, in Response to Atomic Oxygen Irradiation

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Abstract

Utilizing wood in space-based applications poses challenges because the lack of electrical conductivity of this material can lead to local charging while off-gassing under high vacuum can potentially also have adverse effects. However, carbonized wood exhibits electrical conductivity and does not produce gases in a vacuum, making it a potential candidate for use in spacecraft. Even so, erosion by atomic oxygen (AO) at low altitude orbits could potentially degrade wood surfaces. The present study therefore investigated the effects of AO irradiation on carbonized and uncarbonized milled wood lignin (MWL) obtained from both softwood and hardwood sources. The lignin source was found to significantly affect resistance to AO. Specifically, softwood-derived MWL underwent structural changes upon AO exposure whereas hardwood-derived MWL showed greater resistance due to the higher concentration of oxygen-containing functional groups in the latter. AO irradiation evidently induced changes in the carbon

framework while affecting the micropore sizes and peak distribution ranges. These findings highlight the importance of selecting specific wood types and carbonization conditions when producing lignin-derived carbon materials for AO-exposed environments. Softwood MWL is evidently more vulnerable to AO erosion as a result of the guaiacyl structures in this material whereas hardwood MWL resists AO based on its oxygen-rich syringyl groups. The present work underscores the complex relationships between the wood type, concentration of oxygenated functional groups and AO resistance. This research also suggests potential applications for wood-derived lignin carbon in low Earth orbit vehicles and highlights the need for additional studies as a means of better understanding the underlying mechanisms.

Keywords: low Earth orbit, atomic oxygen, wood carbon, milled wood lignin, micropores

1 Introduction

Wood is a sustainable and environmentally-friendly material with a wide range of uses, including in construction, furniture making and paper production. Wood is primarily composed of cellulose, which typically forms crystallized bundles due to the strong hydrogen bonds between the cellulose molecules. Cellulose is typically in the form of lignocellulose surrounded by lignin and the carbonization of this material tends to generate a carbon skeleton. In the case that cellulose is instead present, carbonization first produces lignocellulose which then further reacts to form a carbon skeleton. Lignin, which naturally contains aromatic rings, yields a greater quantity of carbon upon carbonization compared with cellulose or hemicellulose and tends to produce layers of hexagonal carbon structures [1]. Softwood lignins contain guaiacyl nuclei whereas hardwood lignins incorporate both guaiacyl and syringyl nuclei [2]. The lignin in wood is also encapsulated by a carbon skeleton comprising a number of different structures that link the core aromatic groups of lignin to form micropores.

Although wood is recyclable and provides other advantages, the utilization of this resource in space-based applications remains underdeveloped. This is partly because materials used in spacecraft must be conductive to prevent localized charging in response to plasmas and

must exhibit minimal outgassing of volatile compounds that can be hazardous. In particular, it is important that electrostatic discharge (ESD) does not occur as a consequence of the use of a certain material. Because wood tends to release gaseous compounds in a vacuum, there has been limited interest in the use of this material in space. Even so, elemental carbon is lightweight, rigid and resistant to oxidation, all of which are desirable properties for materials employed aboard spacecraft [3-8]. Carbonized wood is also a good conductor and tends not to release gases in a vacuum due to the loss of all volatile organic compound during the carbonization process. However, although carbonized wood lignin has numerous applications [9-14], this substance has not yet been used in space.

At the altitudes associated with low Earth orbit (LEO), approximately 80% of the atmosphere is atomic oxygen (AO), a highly reactive form of oxygen resulting from the disassociation of oxygen molecules in response to ultraviolet radiation. Collisions between AO and satellites travelling at speeds up to 8 km/s can damage the satellite surfaces. In particular, interactions with AO tend to result in the erosion of the polymers that are widely used for thermal protection [15]. The rapid oxidative degradation of such materials is known to occur during exposure to the high concentrations of AO (10^{13} - 10^{15} atoms/cm²) found at LEO altitudes. Surface oxides formed via this process exhibit complex behavior such as the formation of CO and CO₂ [16] and incorporation into the material surface as oxide layers. Interestingly, AO can have effects on various surfaces that differ from those associated with conventional oxidation processes. In fact, the oxidative degradation of materials due to AO can cause significant damage to LEO spacecraft, meaning that the materials of which these craft are constructed must be resistant to the effects of AO [5, 17].

The present study focused on milled wood lignin (MWL), an isolated material often used to examine the structure and reactions of naturally occurring lignin [18]. MWL samples were

initially prepared from Japanese cedar (*Cryptomeria japonica*), a softwood, and Japanese beech (*Fagus crenata*), a hardwood, using conventional methods [19]. These techniques have been described in previous publications [20]. The purity of these MWL samples exceeded 85%, and the chemical structures of these specimens have been described in other papers [20, 2]. Assessments of these specimens highlighted the significant compositional differences between softwood and hardwood sources. As an example, the lignin in the former material (referred to herein as S-MWL) was found to be primarily composed of guaiacyl (G) units, which accounted for 99.5% of the sample, while syringyl (S) units were absent. In contrast, the latter material (H-MWL) comprised 75.2% S and 24.8% G units. The S/G ratios in these specimens were therefore nil and 3.05, respectively, and thus quite different. The carbohydrates found in these lignins, including crystalline and amorphous glucans, xylan, mannan, arabinan and galactan, also varied. Most notably, the xylan concentrations were 64.4 mg/g of cell wall residue (CWR) in the S-MWL and 305.82 mg/g CWR in the H-MWL [21].

It should be noted that the present work did not use isolated lignin as has been the case in many previous studies, but rather employed natural lignin. Prior research by the authors has indicated that, unlike isolated lignin, natural lignin transformed into crystalline carbon with a high degree of graphitization during the carbonization process, resulting in increased electrical conductivity. The aim of this work was to eliminate the effects of other components of the lignin on the pores formed during carbonization and to assess the oxidative degradation of wood carbon resulting from bombardment by AO. For this purpose, experiments simulating AO irradiation were conducted with MWL samples having well-characterized compositions. In the case of the S-MWL in particular, the overwhelming prevalence of G units and the absence of S units offered a unique opportunity to observe AO effects. Conversely, the predominance of S units in the H-MWL provided another distinct chemical environment. These variations in lignin

and carbohydrate composition between the S-MWL and H-MWL represented an ideal framework that established a better understanding of the manner in which AO bombardment affects different wood structures.

A number of analytical techniques were used to investigate the microstructural changes in these materials stemming from AO irradiation. The degradation mechanisms of these carbon-based materials were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) together with Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Through these methods, we aimed to elucidate the distinct behavior of S-MWL and H-MWL upon exposure to AO and examine the implications with regard to potential applications of these materials in space.

2 Materials and methods

2.1 Materials and elemental analyses

As noted in the Introduction, MWL samples were sourced from Japanese cedar and Japanese beech. These samples were prepared using standard techniques [19] and the purity of each was confirmed to exceed 85%. Additional information concerning the chemical characterization of these specimens is available in the literature [20, 2]. The carbon (C), hydrogen (H) and nitrogen (N) contents of the S-MWL and H-MWL were determined using a CHN analyzer (MT-5, Yanako Co., Ltd.) after which the oxygen (O) concentrations were calculated by difference.

2.2 Carbonization of MWL

In each carbonization trial, a 0.01 g MWL sample was placed on a ceramic boat (16 mm wide, 10 mm high and 105 mm long) that was subsequently transferred into a quartz tube

inserted in a programmable tubular electric furnace TMF-300N (AS ONE Co. Ltd., Japan). Carbonization was performed under a flow of nitrogen at 700 °C, using a rate of 23 °C/min to achieve this temperature and a reaction time of 60 min. The yields determined after carbonization were 34 and 28 wt%, respectively, when using the S-MWL made from Japanese cedar and the H-MWL made from Japanese beech.

2.3 AO simulations

The effects of AO were simulated using a CO₂ laser operating at 7 J/pulse in conjunction with a pulsed supersonic valve. This instrumentation comprised a laser detonation source, details of which have been described elsewhere [21]. In these trials, samples of carbonized lignin prepared as described above were placed on a sample holder designed for electron microscopy and various spectroscopic techniques and irradiated with AO using this laser device. Structural changes were examined following a total dose was 2.06×10^{19} atoms/cm². The average collision velocity in this experiment was 6.3 km/s and thus was close to the value expected to occur in orbit. Both carbonized and uncarbonized specimens were treated with AO, alongside control samples which were not exposed to AO irradiation.

2.4 Observations of surface morphologies by SEM

The surface morphologies and microstructures of the specimens were observed using SEM (JEM5310, Japan) at an applied voltage of 15 kV. The carbonized samples were conductive and therefore could be examined by SEM without any effect of charging. However, in the case of non-carbonized samples, gold sputtering was applied to the sample surfaces prior to observation to prevent charging.

2.5 Structural observations by TEM

The microstructures of the samples were assessed using TEM (JEM-2100F, Japan). The applied voltage was 100 kV for the sample without carbonization and 200 kV for those materials subjected to carbonization, to avoid structural changes caused by electron irradiation. A two-dimensional fast Fourier transform was applied to the resulting images to obtain power spectra. These spectra were point-symmetric around their centers, which corresponded to lower frequency components, with higher frequency components associated with those regions further from the center. Each power spectrum was integrated in the rotational direction about its center point to obtain the distribution of interlayer spacing [22].

2.6 FT-IR spectroscopy

FT-IR spectra of the S-MWL and H-MWL materials were acquired in transmission mode over the wavenumber range of 4000–400 cm^{-1} using an FT/IR-4200 spectrophotometer (Jasco, Japan). Dried KBr was used to prepare pellets from the MWL samples and spectra were acquired against a background obtained from a pure KBr disc.

2.7 Raman spectroscopy

The structures of the samples were also analyzed using a Raman spectrometer (Renishaw inVia, UK) equipped with a charge coupled device detector. An argon laser with a wavelength of 514.5 nm was used as the excitation source and spectra were obtained over the range of 1000 to 1800 cm^{-1} . The WIRE 2.0 software package was employed to analyze the resulting spectra. The instrument was calibrated based on the 520 cm^{-1} peak of a silicon wafer.

2.8 Structural analysis using XPS

The chemical compositions and chemical bonding states of the sample surfaces were assessed employing XPS with a Mg $K\alpha$ beam (Shimadzu-Kratos, Japan). These analyses only examined the specimens to a depth of less than approximately 10 nm and thus provided

information solely regarding surface properties. A non-monochromatic Mg K α line (1253.6 eV) source was used and the instrument was operated at 15 kV and 10 mA under a base pressure of approximately 4.93×10^{-7} Pa.

High-resolution narrow C1s and O1s XPS scans were performed with a pass energy of 40 eV and a step width of 0.05 eV. In the case of the uncarbonized samples, a neutralizing gun was used to compensate for the positive charge that accumulated as a result of photoelectron emission. The binding energy values in the spectra acquired from the original and carbonized specimens were calibrated based on the C1s peaks associated with C-C bonds at 285 eV and polycyclic aromatics at 284.6 eV, respectively. All spectra were converted to the kal format using the “dump-dataset” command in the Vision1 software and then to the simple Vamas format in CasaXPS for chemical bonding analysis. Curve fitting was performed with the Gaussian-Lorentz function in CasaXPS. Each C1s peak was found to consist of six components corresponding to peaks related to C1: C-C or C-H at 284.6 eV, C2: aliphatic C at 285 eV, C3: C-OH or C-O-C at 286.1 eV, C4 C=O at 287.6 eV and C5 COOH at 290.1 eV together with C6: a plasmon peak at 291.2 eV.

3 Results and discussion

3.1 Elemental analysis of MWL

The elemental analysis data are presented in Table 1. Both the S-MWL and H-MWL were found to contain essentially no nitrogen and had similar concentrations of hydrogen. The carbon content of the H-MWL was slightly lower than that in the S-MWL. These findings are consistent with previous reports of slightly higher carbon percentages in softwood MWL (such as spruce or pine) of 63-64% compared with hardwood MWL (such as maple, aspen, oak or

birch) of 59-61% [23]. If the ash content of the samples is not considered, these data also suggest that the H-MWL had an oxygen concentration approximately 2% higher than that of the S-MWL.

Table 1. Data from the elemental analysis of MWL specimens obtained from softwood (S-MWL) and hardwood (H-MWL).

Sample	Elemental composition			
	H(%)	C(%)	N(%)	O(%)
S-MWL	5.6	62	0.1	32.3
H-MWL	5.8	59.8	0	34.4

3.2 Observations of surface morphologies by SEM

SEM images of the original S-MWL and H-MWL prior to carbonization are shown in Figure 1. It is evident that the particles of both materials were covered with microfibrils and had similar surface morphologies. A previous study of the same MWL samples used in this study demonstrated that both the S-MWL and H-MWL contained approximately 10% cellulosic glucans [2], which likely formed the microfibrils that were observed.

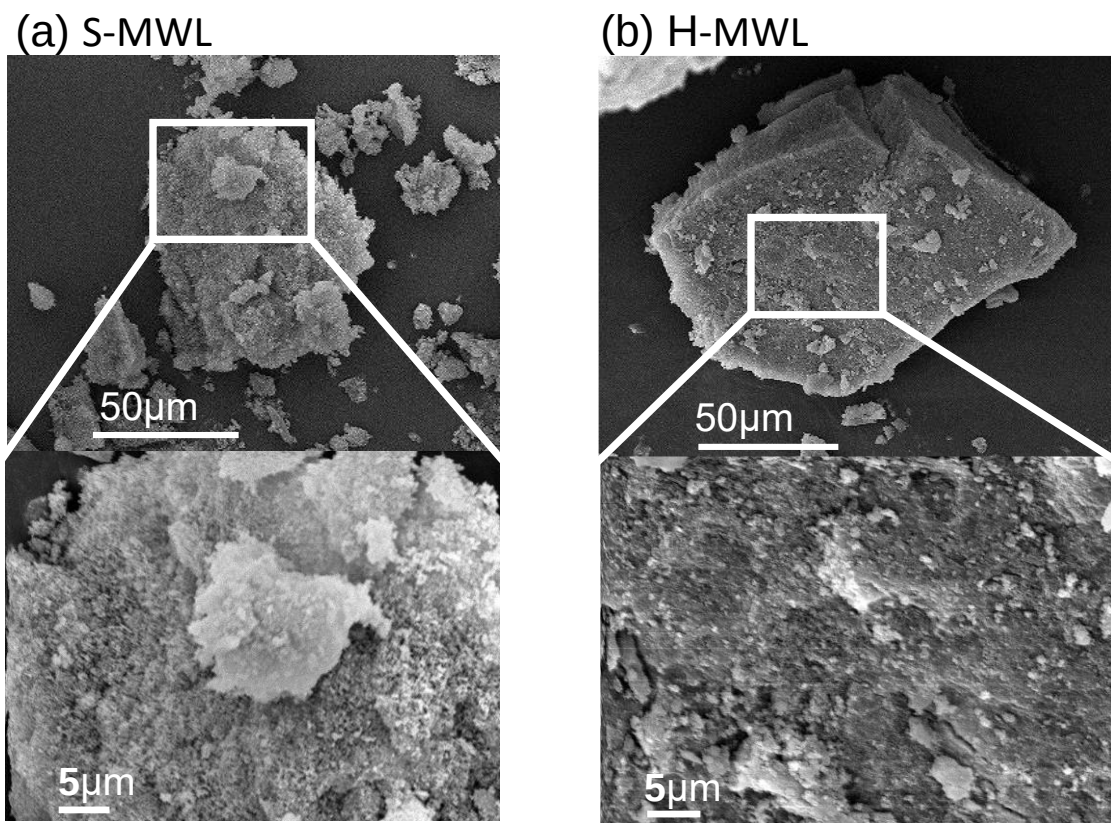


Fig. 1 SEM images of purified milled wood lignin specimens obtained from (a) softwood (S-MWL) and (b) hardwood (H-MWL) prior to carbonization and AO exposure.

SEM images of [uncarbonized](#) S-MWL and H-MWL after AO irradiation are presented in Figure 2. From these images it is evident that numerous microfibrils remained on the S-MWL whereas the majority of the microfibrils disappeared from the H-MWL, exposing a smooth surface.

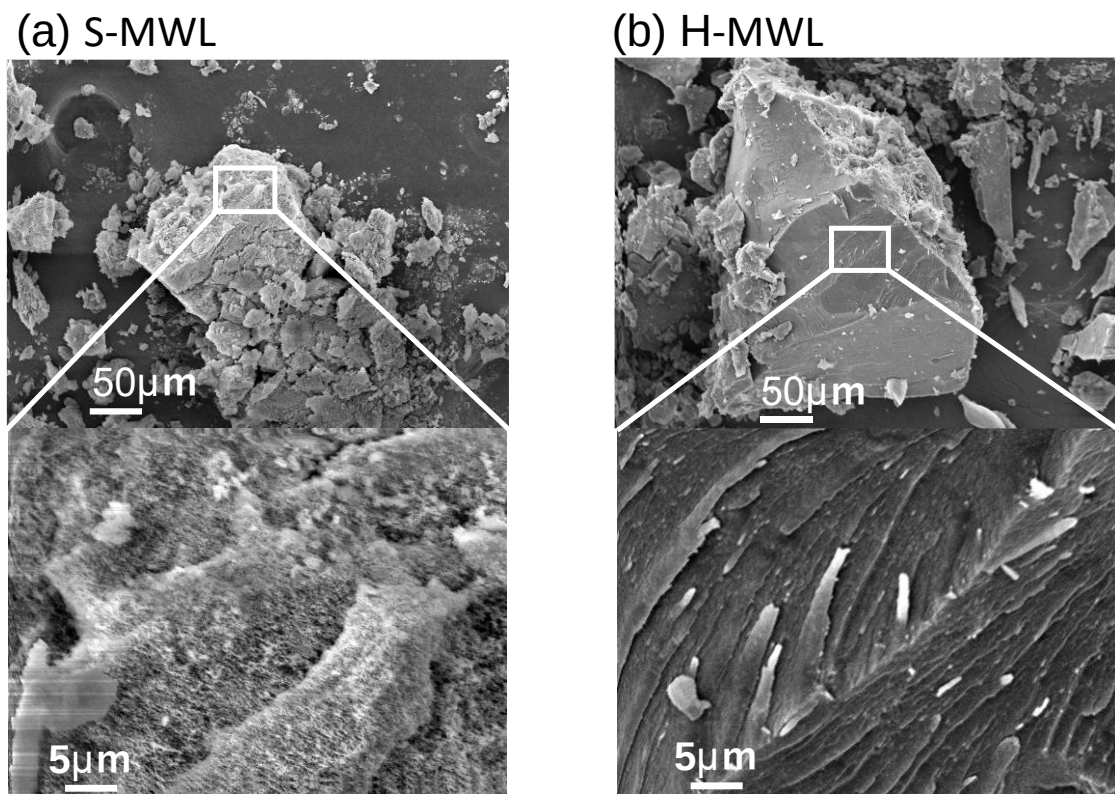


Fig. 2 SEM images of carbonized S-MWL and (b) H-MWL following AO exposure.

The exposure of these materials to AO likely resulted in the vaporization of cellulosic glucan, producing CO or CO₂ [16]. The different surface morphologies of the S-MWL and H-MWL following irradiation can possibly be attributed to variations in the reactivity of the surface microfibers with the AO.

Figure 3 presents SEM images of the S-MWL and H-MWL after carbonization at 700 °C but prior to AO irradiation. Smooth surfaces are apparent, suggesting that the cellulosic glucan microfibers were removed by heating [16]. It should be noted that these MWL materials contained high proportions of aromatic compounds that likely did not undergo volatilization during the micro-graphitization induced by the

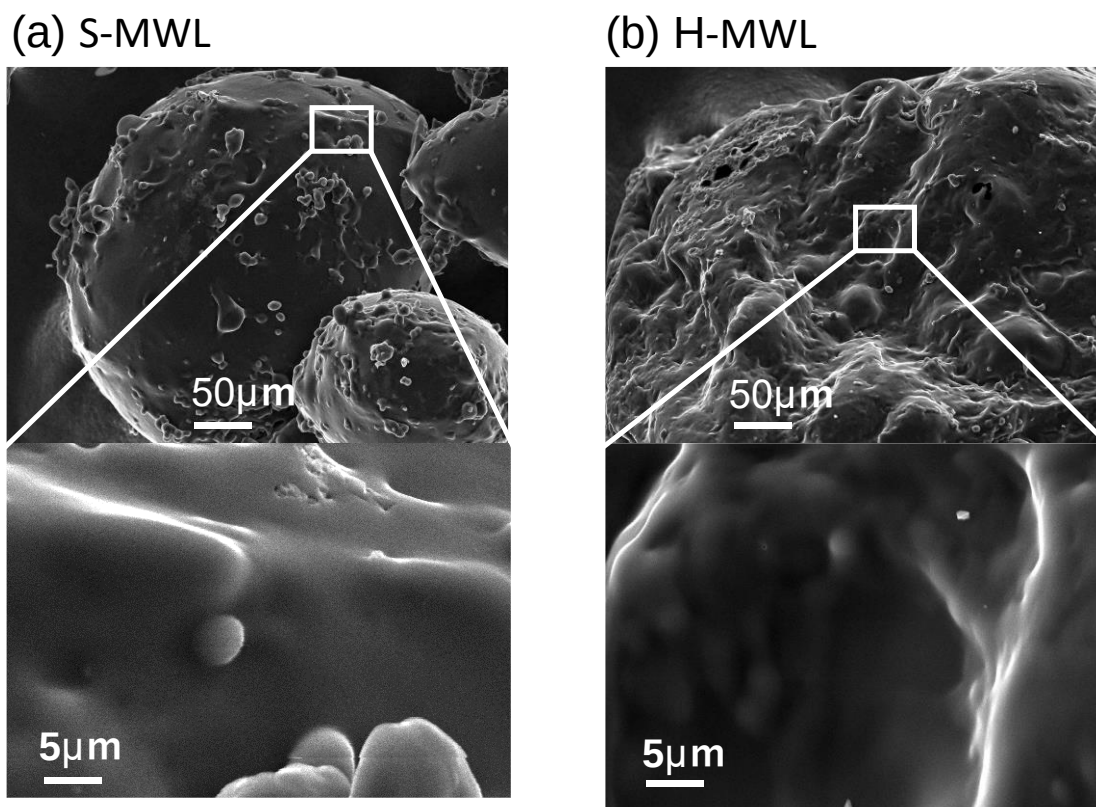


Fig. 3 SEM images of (a) S-MWL) and (b) H-MWL following carbonization at 700 °C without AO exposure.

carbonization process [24].

SEM images of the S-MWL and H-MWL samples carbonized at 700 °C and then irradiated with AO are provided in Figure 4. Numerous pores resulting from surface erosion by exposure to the AO can be seen on the S-MWL. The various chemical reactions occurring at the material surfaces were responsible for the differences in reactivity between the carbonized lignin and AO. These SEM images alone are insufficient to allow a detailed analysis of the reactivity of the carbonized materials with AO. However, it is apparent that interactions between the AO and the MWL were affected by molecular structure, electronic properties and spatial arrangements.

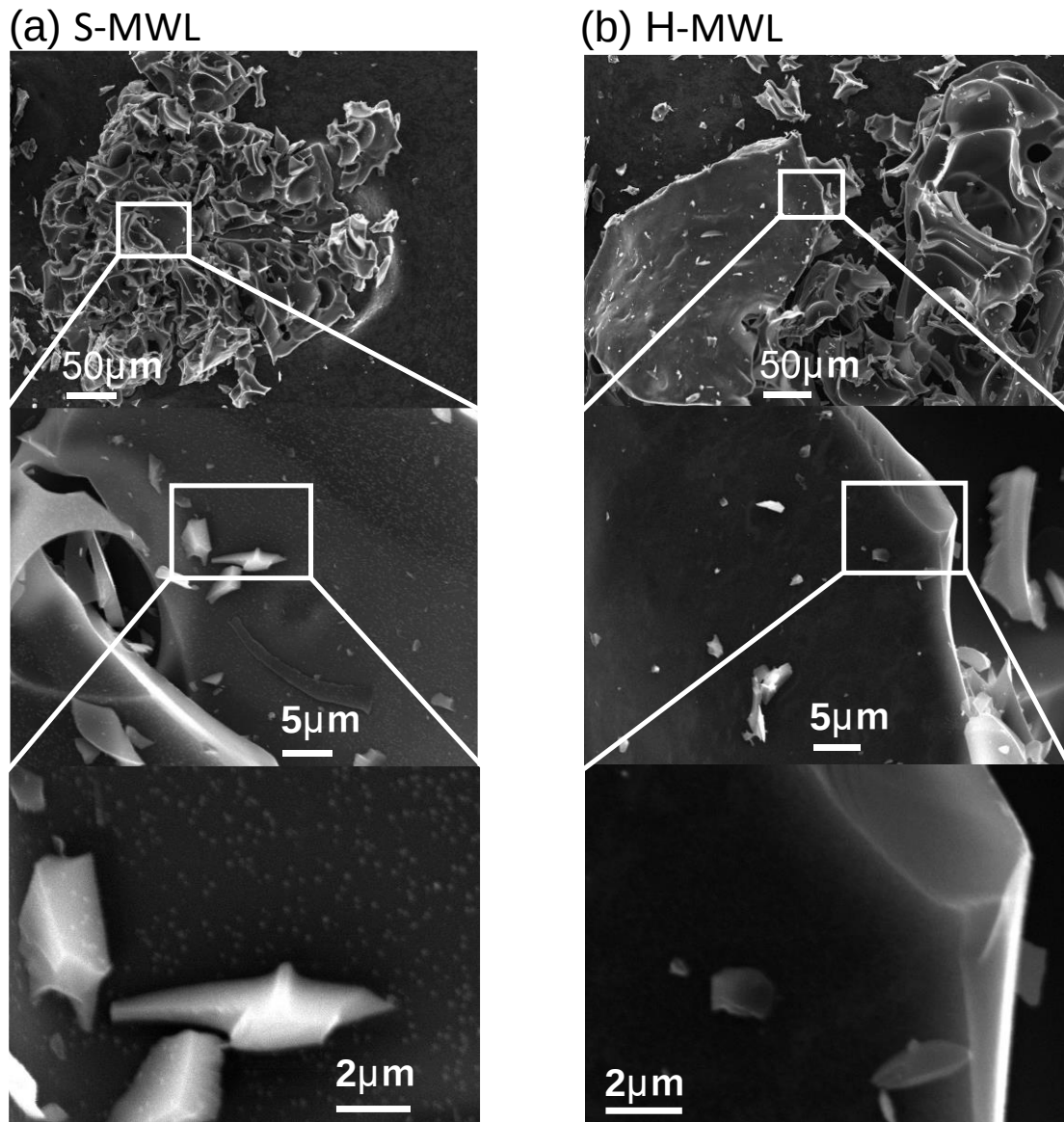


Fig. 4 SEM images of (a) S-MWL (b) H-MWL following carbonization at 700 °C and AO exposure.

3.2 Observations of microstructures by TEM

TEM images of the S-MWL and H-MWL samples both before and after carbonization and before and after AO irradiation are shown in Figure 5. Both materials exhibit the presence of amorphous carbon, indicating that these specimens were made of overlapping planes

comprising short networks of hexagonal carbon structures. In particular, the C sheets consisted of 2-3 layers of hexagonal carbon structures with a total thickness of approximately 1 nm in the H-MWL images [24]. A series of two-dimensional fast Fourier transforms of the TEM images were generated to obtain power spectra (see insets) and the interlayer spacing distributions were obtained by integrating these spectra in the rotational direction. The peak apex values in these graphs were employed to determine the carbon-carbon layer spacing in each case [22]. The layer spacing distributions varied according to the type of lignin in the specimen. This variation reflects the structural differences between the softwood and hardwood lignins both before and after carbonization [20]. The occurrence of multiple spacing peaks indicates imperfect structures. In contrast, the appearance of a single peak following carbonization could demonstrate that this process stabilized the structure, resulting in a more uniform morphology. Hence, different ultra-micropore size distributions were obtained through the linking of aromatic core structures, as reported in reference [22].

Following exposure to AO radiation, the range of pore diameters of the uncarbonized S-MWL changed from 0.442-2.285 nm to 0.698 nm while the range for the uncarbonized H-MWL changed from 0.501-1.220 nm to 0.460-1.169 nm. Treatment with AO caused the uncarbonized S-MWL range to transition from 0.442-2.285 nm to 0.698 nm and that of the uncarbonized H-MWL to go from 0.501-1.220 nm to 0.460-1.169 nm. These data suggest that, while both the S-MWL and H-MWL exhibited

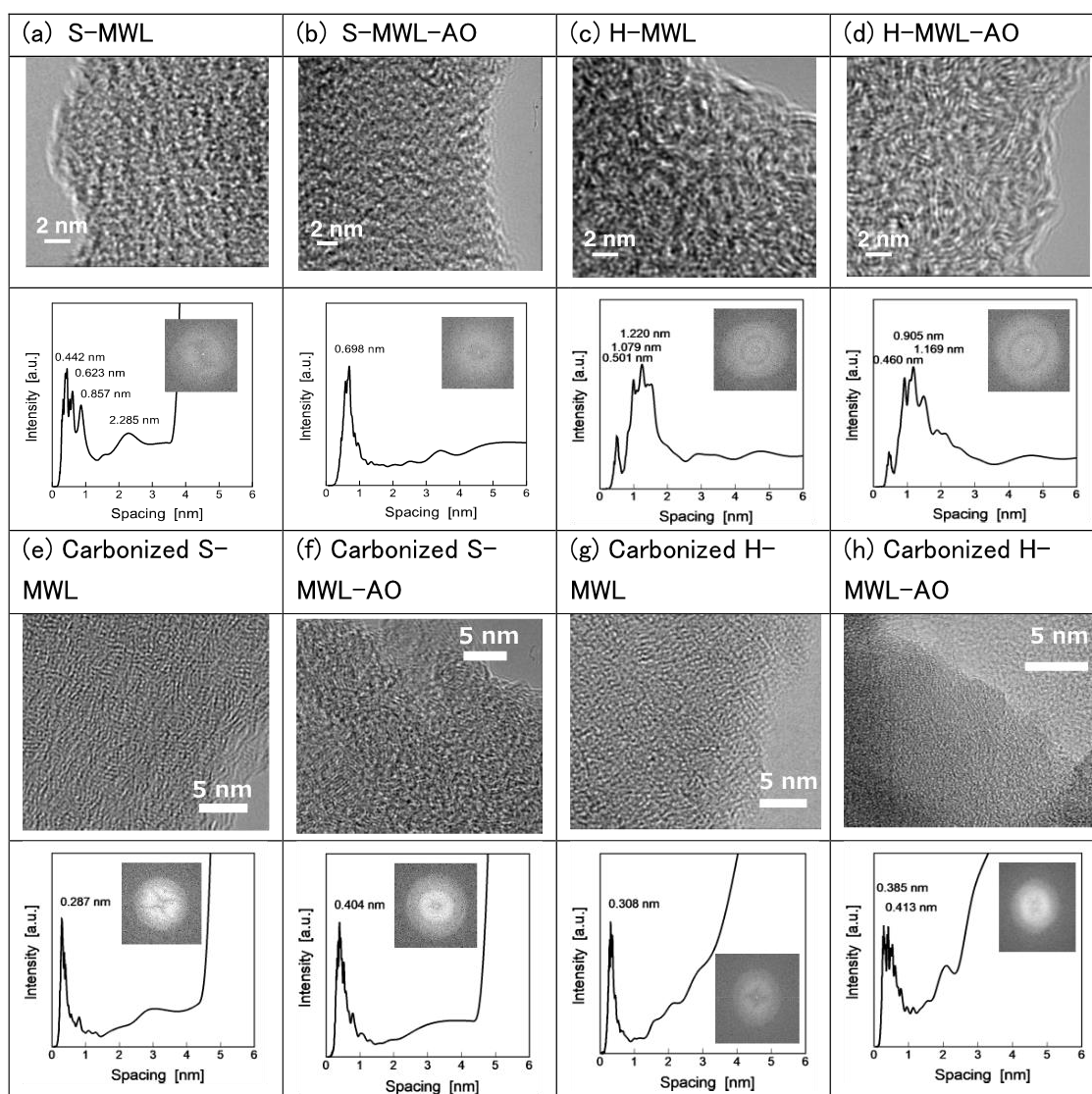


Fig. 5. TEM images, power spectra (insets) and layer spacing distributions of carbonized and uncarbonized S-MWL and H-MWL specimens with and without AO exposure.

increases in layer spacing upon AO exposure, this increase was smaller for the H-MWL.

The average pore diameter of the S-MWL increased from 0.287 to 0.404 nm after carbonization whereas that of the H-MWL changed from 0.308 to within the range of 0.385-0.413 nm. The carbonized S-MWL exhibited decreased layer spacing compared with the H-MWL, suggesting a greater degree of graphitization in the former and longer hexagonal carbon

layer networks. Both the original and carbonized materials showed increases in layer spacing due to AO irradiation although this effect was greater in the case of the S-MWL.

During these trials, a series of reactions occurred that included the adsorption of AO on the pore wall surfaces, leading to oxidation of the carbon surfaces and alterations in the pore microstructure. These changes are believed to have caused the aforementioned peak changes in the average pore diameter. Because surface oxidation would be expected to reduce the strength and functionality of the microporous structure, use of these materials in situations in which high strength is required may not be advisable.

Lignin typically undergoes thermal cross-linking beginning at approximately 200 °C [25] and forms a carbon skeleton at 600 °C, after which molecular movements and reorientation are restricted [26]. These effects result in the creation of micropores between layers that are sandwiched between carbon skeletons. The present work indicated that carbonation without AO irradiation changed layer spacing in the S-MWL from 0.287 nm to within the range of 0.442-0.857 nm while the spacing in the H-MWL went from 0.385-0.413 nm to 0.308 nm. In both cases, the carbonization process decreased the layer spacing and thus extended the hexagonal carbon layer network. In contrast, AO irradiation led to the contraction of this network, which was evidenced from the decrease in layer spacing.

Carbonization and subsequent AO irradiation reduced the layer spacing in the S-MWL from 0.287 to 0.404 nm while that in the H-MWL changed from 0.308 nm to within the range of 0.385-0.413 nm. The data show that AO exposure increased the layer spacing in both the original materials and the carbonized specimens. Conversely, carbonization reduced this spacing. AO irradiation of the carbonized S-MWL produced a slightly large change in layer spacing whereas the H-MWL showed nearly no change. These results demonstrate that the H-MWL had

a more developed graphite structure after carbonization that was less affected by AO irradiation. Hence, hardwood lignin appears to be resistant to the erosion normally caused by AO exposure, as evidenced by the smoother surface morphology observed in the SEM images in Figure 3.

3.3 Characterization of MWL using FT-IR Spectroscopy

The FT-IR spectra acquired from specimens before carbonization and without AO irradiation are provided in Figure 6.

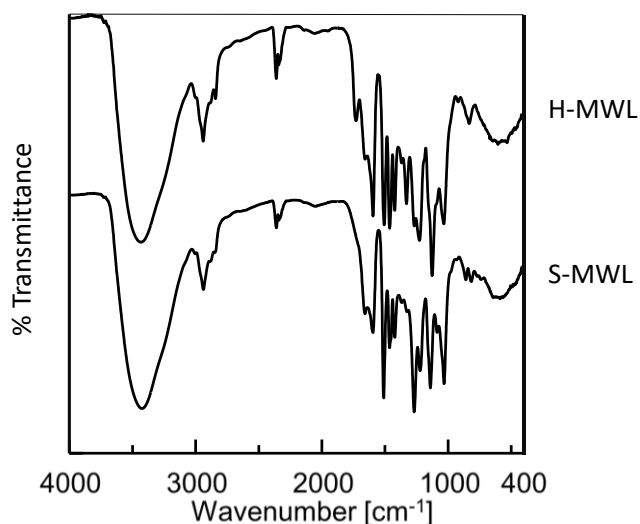


Fig. 6. FT-IR spectra of S-MWL and H-MWL prior to carbonization and AO irradiation.

Both the H-MWL and S-MWL exhibited common features associated with hardwood and softwood lignin, respectively. The H-MWL showed characteristics stemming from its syringyl-propane structure, which is common in hardwood lignin, while the S-MWL spectrum was that expected for a guaiacyl-propane structure, typical for softwood lignin. This analysis confirms the distinct compositional differences between hardwood and softwood MWL and provides some useful insights into the respective functional capabilities of these materials. Specifically, the S-MWL comprised guaiacyl-propane structures that contributed to the

susceptibility of this specimen to AO-induced changes. This susceptibility manifested as notable structural alterations, particularly in the volume and size distributions of micropores.

In contrast, the H-MWL was rich in oxygen-containing functional groups, primarily due to its syringyl-propane structure. This higher concentration of oxygen-bearing functionalities conferred stronger resistance to AO irradiation, both pre- and post-carbonization. Hence, the present hardwood-derived materials demonstrated an increased volume of mesopores with a greater extent of reaction with the AO, illustrating their resistance to AO-induced erosion. Therefore, the inherent properties of MWL, specifically the type of lignin from which the material originates and its functional group composition, dictate the AO resistance. It is obvious that the wood type and carbonization conditions must be carefully considered when developing lignin-based carbon materials for low Earth orbit applications.

3.4 Structural analysis of MWLs by Raman spectroscopy

The Raman spectra of carbonized S-MWL and H-MWL specimens before and after AO irradiation are presented in Figure 7. The D-band, representing the in-plane vibrations of sp²-bonded carbon in incomplete structures, appeared in the range of 1346-1354 cm⁻¹ in the spectra of both the S-MWL and H-MWL. The G-band, associated with the in-plane vibrations of sp²-bonded graphitized carbon, is seen in the range of 1591-1600 cm⁻¹. Various spectral parameters, including D and G band intensities and widths, were obtained after Gaussian curve fitting of the data and are summarized in Table 1. The D band width is a useful measure of the extent of disorder in such materials [25].

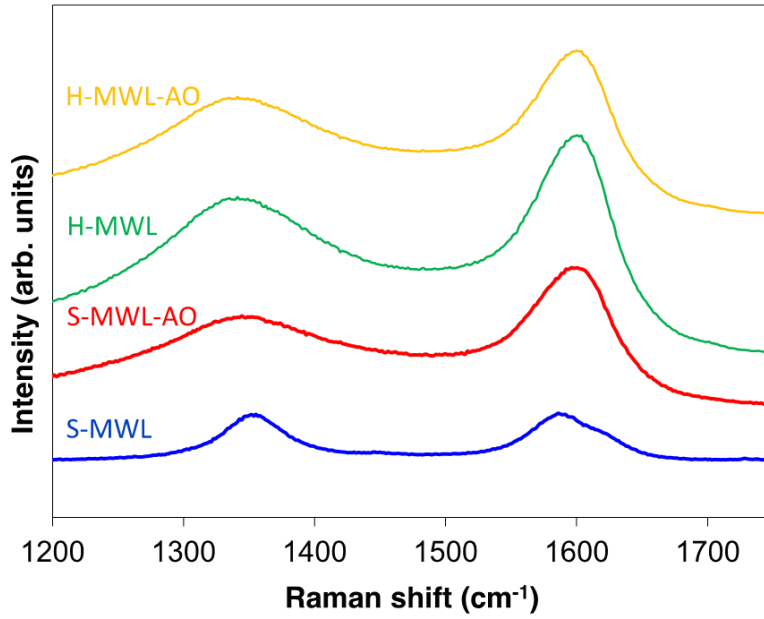


Fig. 7. Raman spectra of MWLs specimens carbonized at 700 °C with or without AO exposure.

A comparison of the D band widths established a greater proportion of structural defects in the carbonized H-MWL compared with the carbonized S-MWL. Moreover, AO irradiation increased the number of structural defects in both types of MWL. These findings were consistent with the results obtained using TEM. The ratios of the intensities of D peaks to G peaks in the various spectra (I_D/I_G) were found to be significantly different between the basal and edge planes. Furthermore, the edge plane ratios varied depending on the polarization direction of the laser. Following AO irradiation, the D band widths of the carbonized S-MWL and H-MWL were found to have increased significantly, from 66 to 87 cm^{-1} and from 148 to 170 cm^{-1} . These results suggest that reactions with AO induced a greater increase in structural defects in the latter. However, these ratios and band widths do not fully explain the development of micro-graphitic structures in these materials. Further research is needed to fully understand the changes in microstructure in response to the various conditions applied in this research.

Table 2. Data from the curve fitting of Raman spectra of carbonized MWL specimens before and after exposure to AO.

Sample	Gaussian band Center (cm ⁻¹)	Bandwidth (cm ⁻¹)	Intensity (Height)	I _D /I _G
S-MWL				1.09
D	1354	66	7.71E+03	
G	1591	77	7.04E+03	
S-MWL-AO				1.15
D	1353	87	8.59E+03	
G	1592	91	7.46E+03	
H-MWL				0.75
D	1346	148	2.23E+04	
G	1598	70	2.98E+04	
H-MWL-AO				0.75
D	1347	170	8.74E+03	
G	1600	68	1.17E+04	

3.5 Structural analysis by XPS

XPS data were obtained as a means of investigating the chemical bonding states of the MWL sample surfaces. Figures 8 and 9 compare the C1s peaks generated by both the original and AO-irradiated S-MWL and H-MWL. It is apparent that AO exposure led to the oxidative degradation of methoxyl groups on the surfaces of the S-MWL, resulting in destruction of the lignin structure. The carbonized MWLs also produced relatively intense C-OH and C-O-C peaks. Exposure to AO apparently generated oxygen-containing functional groups, potentially increasing the O/C ratio for the material.

The change in the spectral shape of the carbonized S-MWL following the AO treatment suggests that the structure of the specimen may have been altered yet still retained characteristics reminiscent of the original structure. This outcome confirms that the structure of this material was more highly affected by AO irradiation, considering that the carbonized S-MWL had fewer oxygen-containing functional groups prior to the AO treatment. The structure of the H-MWL, in contrast, remained largely unchanged by AO irradiation both before and after carbonization. Hence, the abundance of oxygen-containing functional groups on this material

might have provided more resistance to AO. We propose that the carbonization process further stabilized the H-MWL structure, thereby enhancing its resistance to AO irradiation.

In the case of the present XPS data, narrow C1s peaks with small full width at half maximum (FWHM) values indicated a well-defined chemical state while broad peaks with larger FWHM values suggested the presence of chemical impurities, defects

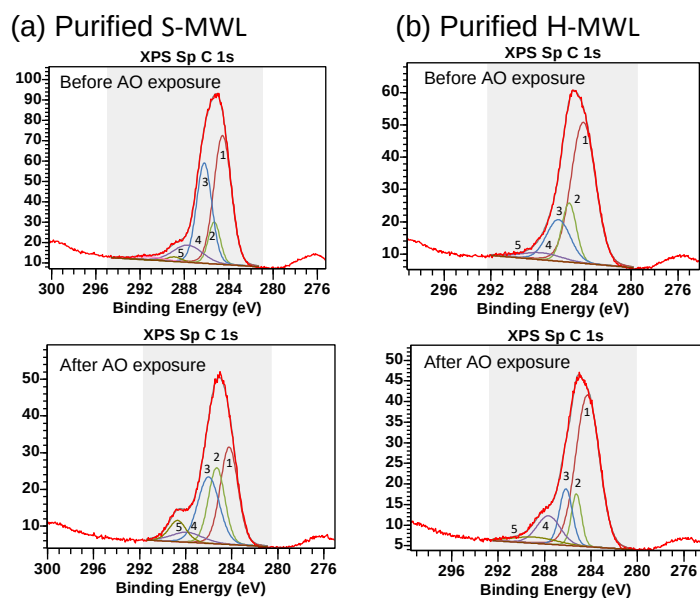


Fig. 8 XPS spectra showing C1s peaks as obtained from uncarbonized (a) S-MWL and (b) H-MWL before and after AO exposure. Legend: 1 = graphitic/aromatic carbon at 284.6 eV, 2 = aliphatic carbon at 285 eV, 3 = C-OH and C-O-C at 286.1 eV, 4 = C-O at 287.6 eV, 5 = COOH at 290.1 eV and 6 = plasmon peak at 291.2 eV [26,27].

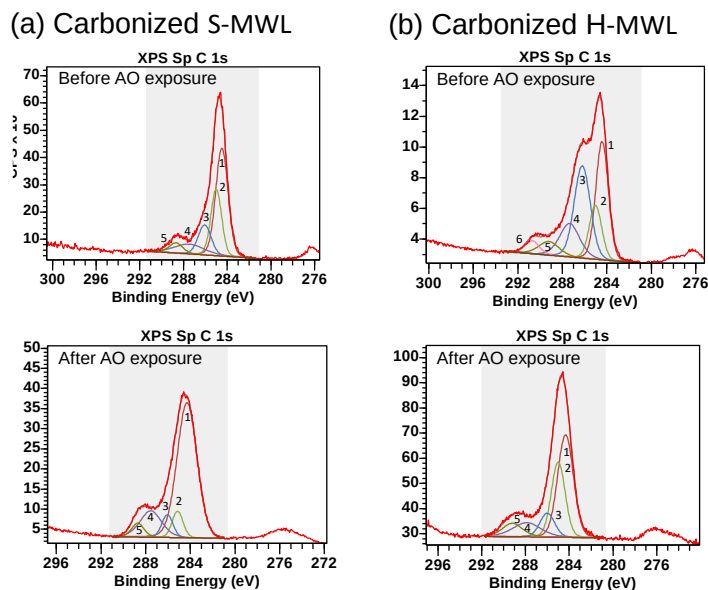


Fig. 9 XPS spectra showing C1s peaks as obtained from carbonized (a) S-MWL and (b) H-MWL before and after AO exposure. Legend: 1 = graphitic/aromatic carbon at 284.6 eV, 2 = aliphatic carbon at 285 eV, 3 = C-OH and C-O-C at 286.1 eV, 4 = C-O at 287.6 eV, 5 = COOH at 290.1 eV and 6 = plasmon peak at 291.2 eV [26,27].

or disorder in the material. Therefore, FWHM values can provide important information concerning the chemical and structural properties of the sample surfaces. Additionally, the O1s/C1s ratios can be used to determine the degree of oxidation of the sample surfaces. Specifically, a higher O1s/C1s ratio indicates a greater concentration of oxygen-containing functional groups on a surface [28] (Table 2).

O1s/C1s ratios and C1s peak FWHM values obtained from XPS data are shown in Table 3. After the AO irradiation process, both the S-MWL and H-MWL exhibited consistent O/C ratios, each recording a value of 0.53. Despite this consistency in the O/C ratios, there was observed variation within the range of 0.42 to 0.57. Furthermore, the Full Width at Half Maximum (FWHM) values showed a decrease for both S-MWL and H-MWL, indicating changes in the peak widths in the respective materials. These changes agree with the TEM images, which established that the layer spacing values in the S-MWL and in the H-MWL were increased as a consequence of both AO irradiation and carbonization. Concurrently, the FWHM

values for the S-MWL and H-MWL decreased from 3.02 to 2.82 and from 3.22 to 3.20, respectively. However, the change in the H-MWL spectra was less pronounced than that in the S-MWL spectra, suggesting that the effects of AO irradiation and carbonization were comparatively minor in the case of the former. These data demonstrate that the H-MWL had a less developed micro-graphitic

Table 3. O1s/C1s ratios and C1s peak FWHM values obtained from XPS data.

Sample	O1s/C1s	FWHM (eV, C1s)
S-MWL	0.42	3.02
S-MWL-AO	0.57	2.82
Carbonized S-MWL	0.33	1.51
Carbonized S-MWL-AO	0.42	2.43
H-MWL	0.53	3.22
H-MWL-AO	0.53	3.20
Carbonized H-MWL	0.25	3.09
Carbonized H-MWL-AO	1.90	1.98

structure that was less sensitive to AO irradiation, as depicted in Figure 5.

Carbonization of specimens not exposed to AO appears to have changed both the O/C ratios and FWHM values for the S-MWL and H-MWL, indicating modifications to surface chemical and structural properties. Specifically, these values were reduced from 0.42 to 0.33 and from 0.53 to 0.25, respectively. Simultaneously, the FWHM values changed from 3.02 to 1.51 for the S-MWL and from 3.22 to 3.09 for the H-MWL. Additional AO irradiation resulted in further changes to the carbonized samples, increasing the O/C ratios from 0.33 to 0.42 and from 0.25 to 1.90, respectively. In addition, in the case of the S-MWL sample, the FWHM value increased from 1.51 to 2.43 whereas that for the H-MWL decreased from 3.09 to 1.98.

A comparison of the layer spacing shows that the S-MWL exhibited a slightly larger change than the H-MWL. This outcome implies that, under identical carbonization conditions,

the micro-graphitic orientation of carbon was less developed in the latter, resulting in an increased concentration of oxygen-based functional groups and reduced sensitivity to AO irradiation. Hence, the H-MWL possessed a structure that was more resistant to erosion by AO irradiation. These results suggest that AO was bound to the MWL surfaces to produce oxygen-based functional groups. This effect would alter the chemical characteristics of the material and also cause physical changes. The increased resistance of the H-MWL to AO is in agreement with the information provided by the TEM images in Figure 5. The exceptionally high O/C ratio of 1.90 for the carbonized H-MWL is noteworthy. The original H-MWL, which contained syringyl nuclei, had a higher number of oxygen-containing functional groups compared with the S-MWL sample. This difference can likely be ascribed to the formation of many oxygen-based functional groups at the edges of the hexagonal carbon layers during carbonization. This hypothesis is supported by the findings from TEM and Raman spectroscopy analyses, as depicted in Figures [5](#) and [7](#).

The effects of AO irradiation and of carbonization on the chemical structures of the S-MWL and H-MWL based on XPS C1s peak areas are summarized in Table 4. Exposure of the S-MWL to AO decreased the C1 (graphitic/aromatic) peak area from 45.4% to 33.8% while increasing the C2 (aliphatic) and C3 (C-OH, C-O-C) areas. In contrast, the H-MWL showed negligible changes in the C1 peak area after AO irradiation but did exhibit changes in other peaks, especially C3 and C4. Additionally, after undergoing carbonization, both types of MWL produced more intense C1 peaks, especially in the case of the S-MWL, for which the peak area was 67.7%. The areas of the C5 (COOH) and C6 (plasmon) peaks also varied with AO irradiation and carbonization but the proportional areas were generally low. These results suggest that AO irradiation and carbonization both greatly modified the chemical structure of the MWL but also that these effects may differ depending on the type of wood. Such results

confirm the critical importance of carefully selecting the appropriate type of wood and carbonization process when manufacturing carbon materials for specific applications.

Table 4. XPS C1s peak areas obtained from S-MWL and H-MWL specimens before and after carbonization and AO irradiation.

Sample	Area of the C1s peak (%)					
	C1	C2	C3	C4	C5	C6
S-MWL	45.4	10.1	31.0	10.2	1.4	2.0
S-MWL-AO	33.8	24.6	28.2	6.2	7.3	0.0
Carbonized S-MWL	46.3	24.9	13.6	10.3	4.9	0.0
Carbonized S-MWL-AO	67.7	7.0	6.2	14.8	4.3	0.0
H-MWL	61.8	15.3	17.9	5.0	0.0	0.0
H-MWL-AO	61.8	9.1	12.7	11.6	4.8	0.0
Carbonized H-MWL	31.1	14.1	31.1	14.0	5.9	3.9
Carbonized H-MWL-AO	42.9	27.5	9.5	10.7	7.3	2.1

S: Softwood, H: Hardwood, MWL: Milled Wood Lignin, AO: Atomic Oxygen. The binding modes and binding energies (eV) for each peak are as follows: C1: Graphitic/Aromatic, 284.6; C2: Aliphatic, 285; C3: C-OH, C-O-C, 286.1; C4: C=O, 287.6; C5: COOH, 290.1; C6: Plasmon, 291.2.

Both the S-MWL and H-MWL exhibited significant susceptibility to AO erosion, independent of their respective crystalline structures. This vulnerability arises from the atomic configurations of these materials, which predispose them to interactions with AO. Nevertheless, the risks of such reactions decrease with the presence of oxygen-containing functional groups that effectively shield the material's carbon atoms from AO exposure [28]. The H-MWL, distinguished by a greater number of structural defects and oxygenated functional groups relative to the S-MWL, demonstrated reduced reactivity with AO. This shielding effect lowered the likelihood of direct interactions between AO and carbon atoms. When subjected to AO irradiation in a low Earth orbit, these materials would still be expected to undergo significant changes at the surface level. The presence of an oxidation layer would also significantly affect reactivity, hence having a critical role in mitigating AO-induced erosion.

Conclusions

The results of the present study highlight the crucial role of the lignin source in determining resistance to AO. S-MWL was found to be more susceptible to AO-induced changes, undergoing significant structural alterations. Conversely, H-MWL showed greater resistance to AO, both before and after carbonization, due to its higher concentration of oxygen-based functional groups. It should be noted that the scope of this study did not include the investigation of different carbonization temperatures. Therefore, our conclusions are most relevant to the specific conditions under which these tests were conducted. These findings stress the importance of carefully selecting the type of wood and carbonization process when creating lignin-based materials for low Earth orbit applications. A complex interplay between carbonization, wood type, oxygen-containing functional groups and AO irradiation is evident. In future research, we plan to supplement with experiments at different carbonization temperatures to further substantiate the conclusions of this study.

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Declarations

Ethical Approval

Not applicable

Competing interests

All authors declare that they have no affiliations with or involvement in any organization or entity with any financial or non-financial interest in the subject matter or materials discussed in this manuscript.

Authors' contributions

Toshimitsu Hata, Sensho Honma and Takeshi Kajimoto conceived the research. Toshimitsu Hata designed the experiments. Toshimitsu Hata, Sensho Honma, Masahito Tagawa and Yuki Tobimatsu performed the experiments and analyzed the data along with Kyoichi Oshida. Toshimitsu Hata, Subyakto and Sensho Honma wrote the manuscript with help from all other authors.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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