Inherently Functionalized Carbon from Lipid and Protein-Rich Biomass to Reduce Ultraviolet-Induced Damages in Bituminous Materials

Amirul Rajib and Elham H. Fini

ABSTRACT: This paper examines the merits of using an inherently functionalized carbon, referred to as biochar as a free radical scavenger. The biochar was made from thermochemical liquefaction of a blend of algae (rich in protein and nucleic acids) and manure (rich in lipid). Here, we studied biochar’s efficacy as a free-radical scavenger and ultraviolet blocker to qualify it as an anti-aging additive in construction, including roofing shingles made from the bituminous composite. The study’s results show that the addition of biochar to bitumen significantly reduced the aging of bitumen. All tested biochars made from various relative proportions of algae and swine manure were found to be effective at reducing the extent of aging; however, the biochar made from algae alone was the most effective. The algal biochar was found to be an effective antiaging additive delaying aging up to 36%, as evidenced by lower rheology and the chemistry-based aging index compared to those of control bitumen after being exposed to the same aging protocol. Algal biochar was found to be more effective than other studied biochar scenarios owing to its inherently functionalized nature. The latter result could be attributed to the high surface area and rich phenol functional groups in algal biochar, turning it into an effective free-radical scavenger. The study outcome highlights the applicability of this inherently functionalized carbon referred to as biochar in construction to enhance sustainability while promoting the circular economy and the biomass value chain.

1. INTRODUCTION

Asphalt aging is implicated in many distresses of materials used in the roofing and paving industry. Bitumen is the glue used in roof shingles and asphalt pavement; aged bitumen has a loss of stress relaxation capacity and an increased propensity to thermal cracking because of excessive hardening.\(^1,2\) Bitumen is part of the asphalt composites used in roofing and pavements, which undergo intense weathering during their service life. The degree of aging of asphalt composites used in roofing and pavements depends on the geographic location, temperature, solar radiation, and the composition of materials.\(^3\) Aging is a prevalent type of failure in asphalt composites used in states with high solar irradiance such as Arizona. Arizona’s annual average direct normal solar irradiance is one of the highest among the 50 states of the U.S.\(^4,5\) Construction materials in Arizona are highly susceptible to accelerated aging because of the combination of high solar irradiance and high temperatures. Increased ultraviolet (UV) radiation decreases the outdoor service life of construction materials such as plastics, rubber, and wood materials.\(^6\) This is especially notable for asphalt composites having high UV adsorption capacity; the UV heats the asphalt matrix and negatively impacts its thermomechanical properties.\(^7,8\) For instance, Hung et al. studied the effect of UV exposure on bitumen by tracking the chemical and morphological changes that occur on the surface of a thin film of bitumen. The authors found that a bitumen film with a thickness of 600 nm became stiffer and lost its viscoelasticity after 20 h of UV exposure performed in an accelerated UV chamber.\(^9\) In another study, bitumen was aged by exposure to combined oxidation and UV radiation, and the changes in the chemical and physical properties of the bitumen were measured; it was found that the aging process led to the formation of conjugated structures and increased the content of fused polyaromatic hydrocarbons.\(^10\) There is a consistent increase of the carbonyl content and loss of saturated hydrocarbons during aging of bitumen.\(^1\)

Several studies tested anti-aging additives and modifiers to delay the aging caused by oxidation and UV exposure.\(^11,12\) For instance, Zadshir et al. used a biomodifier to act as the fog sealant to delay the aging of asphalt; they showed that a biomodifier helped reduce the oxygen uptake of asphalt.
subjected to UV aging. The application of certain polymer modifiers such as styrene–butadiene–styrene (SBS) reduced the rate of formation of carbonyl groups, indicating reduced aging. The addition of specific chemicals to polymer-modified asphalt was found to improve resistance against aging; for instance, the addition of layered double hydroxides to asphalt having SBS was effective in delaying aging, as evidenced by a reduced change in the softening point and flexibility of bitumen during aging.

Among the more recent anti-aging additives are biobased modifiers produced from animal manure, wood pellet, corn stover, and miscanthus; they were all shown to improve bitumen’s resistance to UV aging when added at 10% dosage by weight of asphalt. Furfural, an organic compound, was shown to improve asphalt’s resistance to oxidative aging at a 2% dosage by weight of asphalt. A biomodifier produced from animal waste lowered the viscosity-based aging index of oxidized aged asphalt up to 36% at a 5% dosage of biomodifier. Carbon black is a promising anti-aging additive; the forms with higher surface areas have been shown to be more effective. Amorphous carbon has also been reported effective at reducing the rate of aging in asphalt, as evidenced by lowering the increase in stiffness over time. Among the various forms of carbon that have shown promise as anti-aging additives is biochar. Biochar is an organic compound mainly made from the biomass residue through pyrolysis or liquefaction. The study of biochar in asphalt dates back to a work conducted on the different UV-aged samples. The methods of aging and testing are described in later sections.

2. EXPERIMENT PLAN

Figure 1 shows the experiment plan with the type of tests conducted on the different UV-aged samples. The methods of aging and testing are described in later sections.

2.1. Materials and Methods. The neat asphalt was a PG 64-10 graded asphalt (Table 1). The biochar was produced through thermochemical liquefaction of various dosages of algae and swine manure; details of the thermochemical liquefaction process can be found elsewhere. HTL was performed at 330 °C in a 250 mL stainless steel benchtop batch reactor (Parr Instrument Company, Moline, IL), equipped with a magnetic stirrer, a 4843 controller, and a jacketed heater. The working volume of the system is set to a maximum of 125 mL to facilitate the reactant expansion during the heating process. The biochar was produced at 20% solid loading (25 g dry weight) in all the HTL experiments. For instance, in the case of algae–swine manure scenario (50−50%, respectively), 12.5 g of dry algae and 12.5 g of swine manure were loaded into the reactor after evaluating the moisture content of each sample. The rest of the space was filled with distilled water (100 mL) to make a slurry of the desired solid loading. Once the experiment was completed, the reactor was cooled to room temperature and degassed, and the products were separated using dichloromethane (DCM) as a nonpolar solvent. The solvent was then filtered out to separate the solid residual referred to as biochar. The average particle size of biochar is around 150 μm. The samples were prepared...
by introducing anti-aging agents (biochar) at 5% dosage by the weight of the base asphalt; the two were then blended using a shear mixer at 135 °C for 5 min. The neat asphalt (without biochar) was labeled as 0–0; the first number shows the algae concentration and the second number shows the swine manure concentration in the biomass feedstock that was used to produce the biochar (Table 2). The components of algae and swine manure bio-oil were obtained through gas chromatography—mass spectroscopy (GC–MS) (Table 3) and thin-layer chromatography with flame ionization detection (TLC–FID) (Table 4). More information on compositional characterization can be found elsewhere.24

Table 2. Acronyms of Specimens Used in This Study

| sample name | algae (%) | swine manure (%) |
|-------------|-----------|-----------------|
| 0–0         | 0         | 0               |
| 0–100       | 0         | 100              |
| 20–80       | 20        | 80              |
| 50–50       | 50        | 50              |
| 80–20       | 80        | 20              |
| 100–0       | 100       | 0               |

Table 3. Molecules of Bio-Oil (from GC–MS) from Which Biochar Was Extracted

| molecules                  | % concentration |
|----------------------------|-----------------|
| Algae                      |                 |
| heptane, 2,4-dimethyl-     | 6.7             |
| undecane, 3,7-dimethyl-    | 6.3             |
| octane, 4-methyl-phenol    | 6.1             |
| p-cresol                   | 5.2             |
| 4-ethyl                   | 1.5             |
| phenol                    | 1.4             |
| 4-ethyl-2-methoxy         | 1.1             |
| 4-ethyl-2-methoxy         | 0.6             |

Table 4. Solubility-Based Compounds of Bio-Oil (through TLC–FID) from Which Biochar Was Extracted

| sample | saturates | aromatics | resins | asphaltenes |
|--------|-----------|-----------|--------|-------------|
| 0–100  | 1.93      | 3.06      | 71.24  | 23.76       |
| 20–80  | 0.51      | 2.45      | 8.29   | 88.75       |
| 50–50  | 0.83      | 0.25      | 72.67  | 26.25       |
| 80–20  | 0.00      | 1.31      | 45.09  | 53.60       |
| 100–0  | 0.00      | 15.37     | 83.48  | 1.13        |

2.2. UV Aging Method. The unaged samples were exposed to UV radiation to provide accelerated aging. A QUV-accelerated weathering tester manufactured by the Q-panel company (Cleveland, OH, USA) was utilized to perform the UV aging of the samples. To prepare samples, 10 g of the unaged specimen (biochar and non-biochar) was evenly spread on a steel pan (140 mm diameter) to make a film 0.65 mm thick. The pan was then placed in a UV chamber 10 cm away from the lamp; the lamp used in the UV accelerator had a UV radiation intensity of 0.71 W/m² at 313 nm wavelength. UV exposure continued for 200 h at 65 °C following a method by.26 Samples were collected at time intervals of 50, 100, and 200 h. Figure 2 shows the specimen before and after 50 h of UV aging for 0–0 samples.

2.3. Dynamic Shear Rheometer. The elastic and viscous properties of each sample were measured using an Anton Paar rheometer MCR 302 following the ASTM7175.27 Tests were conducted using an 8 mm parallel plate spindle at a 0.1% strain rate and frequencies ranging from 0.1 to 100 rad/s at 10 °C. Throughout the test, stress and strain were measured, and data were used to calculate the shear modulus (G*) and phase angle (δ) based on eq 1. The complex shear modulus (G*) is a measure of a material’s resistance to deformation when repeatedly sheared, and δ is the time lag between stress and strain. From the data, the modulus and frequency at which the phase angle is 45° were determined as crossover values. At the crossover point, the elastic modulus (G’) and viscous modulus (G”) are equal. It should be noted that the crossover values (frequencies at which storage modulus and loss modulus are equal) are reported to be reliable measures to track changes in the polydispersity of bitumen.29 Considering that progressive aging leads to significant changes in polydispersity as asphaltene molecules forms nanoaggregates,25,30 crossover values are deemed appropriate to not only track the evolution of bitumen during aging but also rejuvenation.31 Provided the crossover frequency and corresponding crossover moduli are measured at the same temperature for all bitumen specimens in comparison, the crossover values can properly detect and compare the extent of aging and in this study extent of delay in aging.

\[ G^* = \frac{\tau_{\text{max}}}{\tau_{\text{max}}} \]

in which

\[ \gamma_{\text{max}} = \left( \frac{\theta r}{h} \right) \] and \[ \tau_{\text{max}} = \frac{2T}{\pi r^3} \]

where \( \gamma_{\text{max}} \) = maximum strain, \( \tau_{\text{max}} \) = maximum stress, \( T \) = maximum applied torque, \( r \) = radius of the sample, \( \theta \) = deflection (rotational) angle, and \( h \) = height of the sample.

2.4. Activation Energy-Based Aging Index. The activation energy of unaged and UV-aged samples was calculated based on the zero-shear viscosity; the activation energy was then used to develop the activation energy-based aging index. To measure zero shear viscosity, rheometry was conducted using a shear rate sweep (using an 8 mm parallel plate with a 2 mm gap) at 50, 60, and 70 °C. The collected data was used to calculate the activation energy using eq 2.

\[ \ln \eta = \ln A + \frac{E_1}{R T} \]
where \( \eta \) is the viscosity of asphalt in Pa·s, \( E_a \) is the flow activation energy (kJ mol\(^{-1}\)), \( R \) is the universal gas constant (8.314 × 10\(^{-3}\) kJ mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature, and \( A \) is the constant.

2.5. Fourier Transform Infrared Spectroscopy. A Bruker FTIR spectrometer (Manufactured by Bruker Corporation) was used to characterize the functional groups of unaged samples and samples subjected to different UV aging levels. Before starting the test, the Fourier transform infrared (FTIR) diamond crystal surface was cleaned with isopropanol. The background spectrum was collected and subtracted from the sample spectra. Each FTIR spectrum was collected from 400 to 4000 cm\(^{-1}\) wavenumbers with a resolution of 4 cm\(^{-1}\) with 32 scans. To analyze the peaks and calculate the area under each peak, the OMNIC version 9.2.86 software was used.

3. RESULTS AND DISCUSSION
The effect of biochar addition on asphalt stiffness was evaluated using complex shear modulus measurements. The mastercurve of complex modulus was developed for all samples (with and without biochar). In order to develop the mastercurve, each specimen was tested at 10, 20, 30, 40, and 50 °C at a 0.1% strain rate and frequencies ranging from 0.1 to 100 rad/s using the dynamic shear rheometer (DSR). The time–temperature-superposition method\(^{13}\) was then used to create a mastercurve at a temperature of 30 °C (Figure 3). As it can be seen in Figure 3, the presence of biochar did not change the stiffness of the asphalt binder.

![Figure 3. Complex Modulus vs reduced frequency mastercurve of all samples.](image)

The following sections present a discussion of asphalt properties as the asphalt undergoes 200 h of the laboratory-aging process.

3.1. Crossover Modulus-Based Aging Index. The crossover modulus-based aging index was calculated for samples aged from 0 to 200 h under UV exposure. Figure 4a,b shows that before aging, all samples show approximately the same value for crossover modulus. The crossover modulus shows a sharp decrease after 50 h of UV aging, and it continues to decrease at a slower rate through 200 h of UV aging. The crossover frequency has the same trend. As shown in Figure 4a,b, asphalt without biochar (0–0) showed the highest change in modulus throughout UV aging. Asphalt samples having biochar showed a lower change in properties compared to the asphalt without biochar, indicating improved resistance to aging because of the addition of biochar. The highest resistance to UV aging (the lowest aging index) was found for the asphalt having biochar made from algae alone (the sample referred to as 100–0, algae–manure ratio). The data was used to calculate the aging index using eq 3 for each scenario (Table 5). As shown in Figure 5, the constant resistance through 200 h of aging can be achieved by introducing algal biochar.

Rheological aging index

\[
\text{Rheological aging index} = \frac{\text{unaged crossover modulus} - \text{aged crossover modulus}}{\text{unaged crossover modulus}} \times 100
\]  

(3)

To further evaluate the aging rate for each aging interval (0–50, 50–100, and 100–200 h), the change of the crossover modulus and crossover frequency during the aging interval was determined using the slope of the plot at each aging interval (Figure 5). As shown in Figure 5, the aging rate of asphalt without biochar was found to be higher than all the asphalt samples having biochar. Asphalt samples having biochar performed differently depending on the type of biochar they had. The lowest aging rate (highest resistance to UV aging) was found for biochar made from algae alone (the 100–0 sample).

3.2. Activation Energy-Based Aging Index. Figure 6 shows the activation energy plot for all samples after UV aging of 0 to 200 h. As shown in Figure 6, the presence of biochar increased the activation energy as expected because the asphalt became stiffer overall when biochar was present. However, to study the aging effect, the change of properties during each aging period was monitored. The data was used to calculate the activation energy-based aging index using eq 4 for each scenario (Table 6). Neat asphalt had an increase in activation energy of 9% after 50 h and 14% after 200 h (Table 6). Among asphalt samples that contained biochar, the algal biochar had the lowest increase in activation energy of 2.48% after 50 h and 5.56% after 200 h. The 5.56% increase after 200 h represents a 61% reduction compared to the 14.36% increase for asphalt without biochar after 200 h aging.

Activation energy-based aging index

\[
\text{Activation energy-based aging index} = \frac{\text{aged activation energy} - \text{unaged activation energy}}{\text{unaged activation energy}} \times 100
\]  

(4)

To evaluate the aging resistance of biochar, the aging rate was defined as the slope of each segment (0–50, 50–100, and 100–200 h); these slopes are plotted in Figure 7. As shown in Figure 7, the aging rate was the highest for the 0–0 sample, and all samples with added biochar showed a lower aging rate compared to the neat sample. Figure 7 also shows that the highest aging rate occurs during the first 50 h of aging, and the...
rate of change in activation energy slows during the subsequent intervals.

3.3. Chemical Aging Index. FTIR spectroscopy was used to track the extent of change in the chemical structure of asphalt during aging. To quantify the change, eqs 5 and 6 were used to calculate the carboxyl functional groups and sulfoxide functional groups of all samples, following the method used in ref 33. The carbonyl and sulfoxide index results for specimens exposed to UV aging are shown in Figure 8.

Carbonyl index

\[
\text{Carbonyl index} = \frac{\text{area under curve from 1680 to 1800 cm}^{-1}}{\text{area under curve from 600 to 4000 cm}^{-1}} \times 1000
\]

(5)

Sulfoxide index

\[
\text{Sulfoxide index} = \frac{\text{area under curve from 960 to 1050 cm}^{-1}}{\text{area under curve from 600 to 4000 cm}^{-1}} \times 1000
\]

(6)

Table 5. Crossover Modulus-Based Rheological Aging Index

| Aging index % for 0–50 h | 0–0 | 0–100 | 20–80 | 50–50 | 80–20 | 100–0 |
|--------------------------|-----|-------|-------|-------|-------|-------|
| 0–50 h                   | 28.17 | 18.92 | 19.03 | 20.84 | 21.87 | 17.45 |
| Total aging index %      | 44.96 | 31.09 | 34.31 | 32.85 | 29.93 | 24.75 |

Table 6. Activation Energy-Based Aging Index

| Aging index % for 0–50 h | 0–0 | 0–100 | 20–80 | 50–50 | 80–20 | 100–0 |
|--------------------------|-----|-------|-------|-------|-------|-------|
| 0–50 h                   | 9.49 | 4.63  | 5.70  | 4.38  | 4.69  | 2.48  |
| Total aging index %      | 14.36 | 8.54  | 9.95  | 8.26  | 8.08  | 5.56  |

Figure 4. Crossover modulus (a) and crossover frequency (b) values for different aging levels.

Figure 5. Aging rate calculated based on the slope of crossover modulus (a) and crossover frequency (b) values as a function of aging time.

Figure 6. Activation energy plot for all samples through 200 h of UV aging.
As shown in Figure 8, all samples had similar values for the carbonyl index and sulfoxide index before aging because the presence of biochar did not contribute to either of the above indexes before aging. When asphalt samples were exposed to UV aging, their carbonyl index and sulfoxide index increased, with the largest increase happening in the first 50 h. Asphalt samples without biochar showed a higher increasing rate than asphalt samples with biochar. To facilitate comparing studied scenarios, the sum of the two indexes was calculated at each aging interval and referred to as the chemical aging index (CAI), following the method used by other researchers.28−30 The asphalt sample without biochar showed a CAI of 22% after 50 h and 40% after 200 h of aging (Table 7). Among all asphalt samples with biochar, the sample containing algal biochar (100−0 scenario) had the lowest CAI value of 17% after 50 h and 26% after 200 h of aging. This represents a 36% improvement in the aging resistance of asphalt because of the addition of algal biochar. Figure 9 shows the aging rate based on changes in the CAI over time.

As shown in Figure 9, the CAI-based aging rate was consistently lower for asphalt samples with biochar compared to those without biochar. The findings are in line with other studies showing the benefits of carbonaceous nanoparticles in delaying asphalt aging.9,33

Finally, all the aging indexes calculated for different aging levels for the sample with no biochar and the sample with algal biochar (100−0) are summarized in Table 8.

Table 7. CAI (%)a

|        | 0–00 | 0–100 | 20–80 | 50–50 | 80–20 | 100–0 |
|--------|------|-------|-------|-------|-------|-------|
| CAI (%) | 21.75| 21.11 | 18.29 | 17.17 | 17.08 | 16.69 |
| CAI (%) for total 0–200 h | 40.36| 38.62 | 29.82 | 28.34 | 28.61 | 25.91 |

aCAI = carbonyl index + sulfoxide index.

Table 8. Summary of Calculated Aging Indexes after 200 h of UV Aging

|                  | rheology aging index | activation energy-based aging index | CAI |
|------------------|----------------------|-------------------------------------|-----|
| no biochar (0–0) | 44.96                | 14.36                               | 40.36|
| algal biochar (100–0) | 24.75               | 5.56                                | 25.91|
| % improvement    | 45                   | 61                                  | 36  |

Figure 7. Activation energy-based aging rate (slope of activation energy graph).

Figure 8. (a) Carbonyl index and (b) sulfoxide index values for all samples exposed to UV aging.

Figure 9. CAI-based aging rate based on the slope of CAI during each time interval.
4. CONCLUSIONS
This study examines the efficacy of several biochars made from various ratios of algae and swine manure as anti-aging additives to delay asphalt aging. The extent of aging was tracked based on changes in the physicochemical properties of asphalt samples containing 5% of each biochar. The physicochemical properties were measured using rheological measurements, chemical fingerprints, and activation energy of each sample to determine the aging index. The aging index was quantified at several intervals during 200 h of UV radiation. All indexes showed that asphalt samples containing biochar had significantly lower aging levels compared to samples without biochar, indicating that the presence of biochar delays UV aging. This was attributed to the biochar’s capability as a free-radical scavenger and UV blocker. Among asphalt samples that had biochar, the one with algal biochar showed the highest resistance to UV aging. This was attributed to algal biochar’s having the highest content of phenolic structures, contributing to its role as a radical scavenger. The results showed that with the addition of algal biochar, the improvement in aging indexes after 200 h of UV aging was 45% for the rheological aging index, 61% for the activation-energy-based aging index, and 36% for the CAl. The latter biochar named as UV cut found to be promising for use bituminous composites to extend their service life by delaying their aging, especially in areas with high solar irradiance. The study outcomes highlight the applicability of biochar to enhance sustainability in construction and promote the circular economy.

■ AUTHOR INFORMATION
Corresponding Author
Elham H. Fini — Arizona State University, Tempe, Arizona 85287-3005, United States; orcid.org/0000-0002-3658-0006; Email: efini@asu.edu

Author
Amirul Rajib — Arizona State University, Tempe, Arizona 85287-3005, United States; orcid.org/0000-0002-9567-8986

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03514

Notes
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