

Development of Eco-Friendly Antifungal Coatings by Curing Natural Seed Oils on Wood

*Cathy C. Tang, Ying Li, Leman Kurnaz, and Jie Li**

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Corresponding Author Email: [LI439@mailbox.sc.edu \(Jie Li\)](mailto:LI439@mailbox.sc.edu)

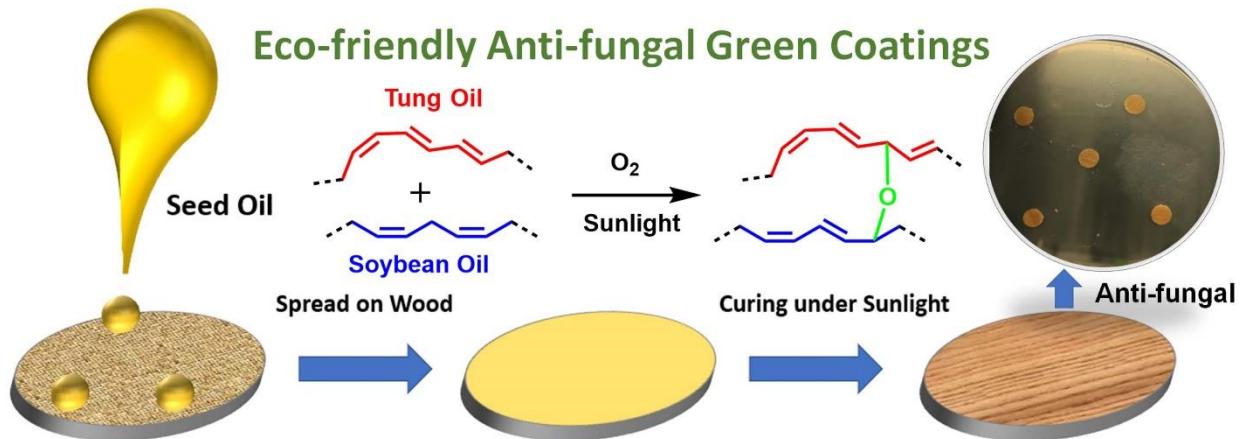
Abstract

Protective green coatings are advantageous because they are eco-friendly and sustainable. In this study, three natural seed oils, tung, linseed and soybean, were used to investigate how coatings with different oil compositions could inhibit fungal growth. The oils were placed under direct sunlight to form cured films on maple wood. The curing chemistry and its effect on chemical resistance, water resistance and thermal stability were characterized and evaluated by FTIR, ^{13}C NMR, solvent immersion, water contact angle and thermogravimetric analysis. The oil-coated samples were then placed on agar petri dishes that were spread with white-rot fungi. The areas of growth inhibition were measured over several days using an agar diffusion assay. The results showed that all oil-based coatings inhibited the fungus causing white-rot disease, with tung oil being the most effective followed by linseed and soybean oils. By mixing with a small fraction of tung oil, both linseed and soybean oils showed curing rates at least two times faster than individual oils and demonstrated much better inhibition of growth against fungi. This class of green natural seed oil coatings could be beneficial both economically and socially, given their high abundance, low cost, and environmental friendliness.

Highlights

- New coatings based on natural seed oils, tung, linseed and soybean, are developed for inhibition of fungal growth.
- Mixed seed oils show more efficient curing, two times faster than soybean and linseed oils.
- Antifungal potential of the seed oil coatings is demonstrated.
- Fractional addition of tung oil enhances resistance and durability of soybean or linseed oil to fungal growth.

Graphical Abstract



Keywords

Eco-friendly coatings; Antifungal; Natural seed oils; Curing

1. Introduction

Green coatings are in high demand driven by government regulations and consumer interests[1-3]. The general public continues to use coatings with reducing volatile organic compounds (VOCs), which are harmful to the environment and human health[4]. The U.S. Green Building Council certifies a green building program called LEED (Leadership in Energy and Environmental Design), which further drives the demand for green coatings[5]. With stringent environmental regulations, there has been a growing interest in utilizing renewable natural resources as candidates for manufacturing eco-friendly coatings[6, 7]. On the other hand, there is a societal and economical need for anti-microorganism materials that can act as protective coatings against mold growth on commonly used surfaces including wood[8-10]. Natural seed oils have been historically used as paints and coatings to prevent wood rotting[11, 12]. In Southeast Asia, tung oil was traditionally used as a protective agent against microorganism growth on ancient wooden ships that traveled across rivers, lakes, and oceans[13, 14]. Even though tung oil is historically successful in its use as a protective coating, it has several limitations: it is predominantly produced in Asia and scarcely available in other places. Its chemical composition is unique, not present in most other oils. Due to these restrictions, other seed oils could be more appealing as alternative coatings to prevent mold growth on wooden surfaces, as they are much more abundant and widely accessible[15].

Seed oils have similarities in chemical structures as they consist of triglycerides with unsaturated fatty acids[16]. Representative oils used in this study are shown in **Figure 1**. However, the major compositions and percentage of double bonds differ between seed oils. Tung oil is made up of over 82% alpha-eleostearic acid containing three conjugated double bonds. Conjugated double bonds allow an oil to cure faster than unconjugated double bonds. Unlike tung oil, other seed oils are made of a mixture of saturated, oleic, linoleic, or linolenic fatty acids covalently linked together. For example, both linseed and soybean oils are made up of multiple double bonds, but not conjugated. Linseed oil is made of 53% linolenic acid containing three unconjugated double bonds, while soybean oil contains 58% linoleic acid with two unconjugated double bonds. The lack of conjugated double bonds has historically made both soybean and linseed oils less appealing for coating applications than tung oil.

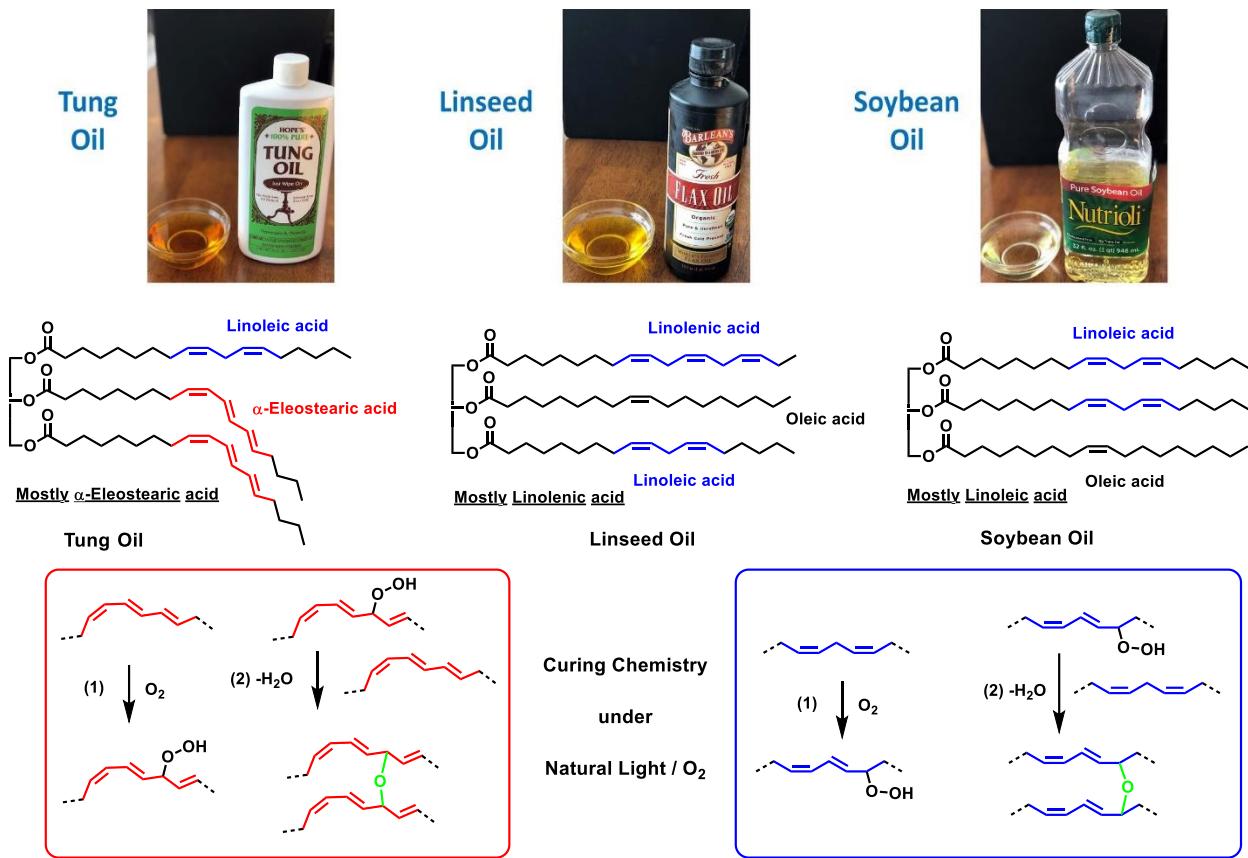


Figure 1. The compositions of three seed oils used in this study and respective curing chemistry under natural sunlight.

During the curing process, the oil hardens through a chemical reaction in which the components crosslink and polymerize through the action of oxygen[17, 18]. The curing chemistry of oil can be seen in **Figure 1**. This process begins when an oxygen molecule (O₂) is linked (inserted) into adjacent carbon-hydrogen bonds that are next to one of the double bonds within the unsaturated fatty acid. The linked oxygen and carbon-hydrogen lead to the formation of hydroperoxide that causes bonds to link between neighboring fatty acid chains, ultimately resulting in a polymerized chain network. This polymerization is what gives the cured seed oils a hard and durable film, making it a protective paint (coating). During these processes, radicals are typically generated. Whatever the structures can stabilize the formation of radicals could accelerate the curing. In this regard, conjugate double bonds are superior to allylic double bonds, which are better than an isolated double bond[19].

Herein we report a comparative study on the use of natural seed oils to prepare eco-friendly antifungal green coatings. Towards this goal, three oils were chosen: tung oil, linseed oil, and

soybean oil. Tung oil has been the most successful drying oil because of its protective waterproof finish. Though linseed and soybean oils are much less used as antifungal coatings historically, they could be potential alternatives to tung oil due to the presence of multiple double bonds in their chemical structures. The knowledge gained from this comparative study was further expanded to explore the mixing of two different oils. It is quite surprised that very little efforts have been devoted to the quantitative antifungal research, even including tung oil, not to mention soybean oil, even though it is the second most abundant plant oil. This study could pave a new avenue to enhancing the value of vastly abundant seed oils with the aid of tung oil.

2. Materials and Methods

2.1. Materials

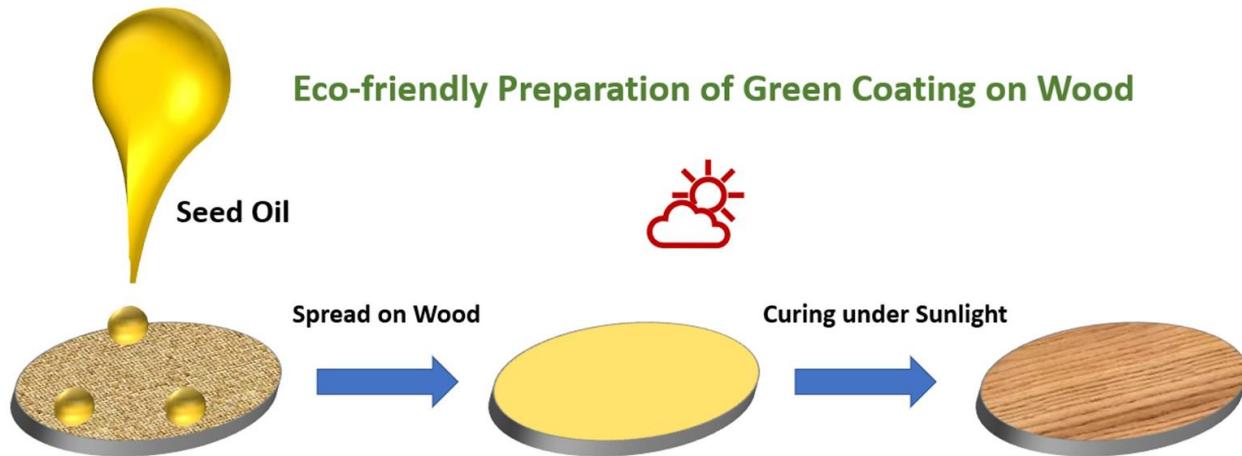
All-natural HOPE'S 100% pure tung oil, Barlean's fresh organic flax oil, and all-natural soybean oil were purchased from Amazon.com. Untreated veneer maple wood (3.175 mm thick) was purchased from Woodcraft Supply and was precut cut into 10 × 10 cm square panels. White-Rot fungus (*Phanerochaete chrysosporium* ATCC® 24725™) was purchased from ATCC.

2.2. Characterization

Fourier Transform Infrared Spectrometry (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer incorporated with a diamond crystal plate as the reflector. Measurements for each sample were collected over the spectrum range of 4000-600 cm⁻¹ with 24 scans. Both liquid seed oils and solid cured oil samples were used for measurements. Nicolet iS5 FTIR spectrometer with iD7 ATR accessory was used to directly record spectra of coatings on wood samples. Solid state ¹³C CP-MAS Nuclear Magnetic Resonance (NMR) spectra were collected on a Bruker Avance III-HD 500 MHz spectrometer fitted with a 1.9mm MAS probe. The spectra were collected at ambient temperature with sample rotation rate of 20 kHz. 2 ms contact time with linear ramping on the ¹H channel and 62.5kHz field on the ¹³C channel were used for cross polarization. ¹H dipolar decoupling was performed with SPINAL64 modulation and 145kHz field strength. Free induction decays were collected with a 20 msec acquisition time over a 350 ppm spectra width with a relaxation delay of 2s. Thermal stability of cured oils was carried out with thermogravimetric analysis (TGA) using a TGA Q5000 system (TA Instruments), ramping from

50 to 800 °C at 10 °C/min under nitrogen gas atmosphere. The decomposition temperature (T_d) was determined at 5% weight loss.

Scheme 1. Illustration of a procedure to prepare seed oil-coatings on wood. The seed oils are spread across the wood samples and then cured under direct sunlight.



2.3. Seed Oil Curing

Maple wood was first cut into 10×10 cm squares. The wood samples were then placed into petri dishes, wrapped with aluminum foil, and autoclaved. 600 μL of each individual seed oil (tung, linseed, soybean) was spread across the entire maple wood. For each type of seed oil, there was also one control, a plain 10×10 cm maple wood sample without oil coating. These 10×10 cm samples were then placed in petri dishes, which were wrapped with Parafilm. These samples were placed outdoor under direct sunlight to begin the curing process. **Scheme 1** illustrates the process of seed oils being spread on wood and cured under direct sunlight. This process lasted for 2-3 weeks until the oils cured adequately. Once the oils formed a protective coating, each cured sample of wood was cut with an autoclaved hole puncher into circular disks, each with a diameter of 7 mm for different oil-coated maple wood.

2.4. Water and Solvent Resistance

The chemical resistance of cured oils was examined at 25°C. Oil samples were analyzed in different solvents by an immersion method. Acetone, hexane and water were used. Samples were

weighed in the range of 10-30 mg for each experiment. m_i is designated as the initial mass. The samples were immersed in 1 mL of the corresponding solvent for two days. The samples were then taken out, cleaned with Kimwipes to remove solvent on the surface, and then weighed. m_s is designated as the swollen mass. Lastly, these swollen samples were placed in a vacuum oven at 50°C overnight to remove any remaining solvents. The final mass is designated as m_f . Soluble fraction and swelling ratio were calculated according to the following equations:

$$\text{solubility ratio (\%)} = \frac{m_i - m_f}{m_i} \times 100; \text{swelling ratio (\%)} = \frac{m_s - m_i}{m_i} \times 100$$

2.5. Water Contact Angle

Static water contact angles were measured using a VCA Optima system (AST Products, Inc) with a manual controller capable of casting 1 μ L of Milli-Q water droplets. Static contact angles were recorded right after placing the water drop on the surface.

2.6. Agar Preparation

A 2000 mL Erlenmeyer flask with a sterile stir bar inside was placed on a magnetic stirrer. 1000 mL H₂O, 20 g glucose, 10 g peptone, 5 g yeast extract, and 17.5 g agar powder were respectively added into the flask in 2-minute intervals. After the agar solution was mixed for 2-3 minutes, aluminum foil was wrapped around the Erlenmeyer flask and placed inside an autoclave for 1 hour. Then, 20 mL of agar solution was poured into each petri dish. The solution was left to harden for 30 minutes in a BSL-2 hood and then placed in a refrigerator at 4 °C.

2.7. Fungal Growth and Inhibition

A stock solution of white-rot fungus was first prepared. A serial dilution was carried out. A plastic vial was filled with 900 μ L PYG (peptose, yeast extract, and glucose) solution. 100 μ L of the stock solution of white-rot fungus was transferred into the plastic vial already filled with 900 μ L of PYG solution. Then, 100 μ L from the first vial was transferred into another vial pre-filled with 900 μ L PYG solution. Once the serial dilution process was completed, 100 μ L of the new fungus solution was added to the surface of each agar petri dish. Eight to ten solid sterile glass beads were placed inside each petri dish and shaken back and forth to spread fungi across the surface.

Oil-coated wood disks were then placed on the surface of white-rot fungi-coated agar dishes, which were then securely wrapped with parafilm. The samples were placed in an incubator

preset at 32 °C, where the fungi grew. The process of the fungal growth could be observed over time. It is worthy to note that the growth speed should be carefully balanced. If the fungi grow too fast, it would be challenging to observe the difference among different oil coated samples. One of possible approaches was to let the fungi grow at 20-25 °C after the first 24 hour at 32 °C.

3. Results

3.1. Curing of individual seed oils

The preparation of green coatings relies on two renewable resources: natural seed oils and direct sunlight. The straightforward process is VOC free. Tung oil is usually considered as a golden standard among drying oils. Linseed oil possesses rich linolenic acid, which is the next in line preferred for curing after eleostearic acid. Soybean oil is the second most abundant plant oil. Maple veneer was chosen as the wood substrate for coating, which can be cut into thin disks for later evaluation on fungal growth. Each oil was separately spread onto the wood surface and then subject to direct sunlight exposure for about two to three weeks. Tung oil typically stopped flowing after only 1-2 days under sunlight, while linseed and soybean oils would take 3-4 days and one week, respectively. To facilitate better observation, oils were also placed into aluminum foils. The curing was observed with the distinct change of liquid oils into solid materials, as shown in **Figure 2A**. The cured oils change from nearly colorless transparent in soybean to yellow opaque in tung.



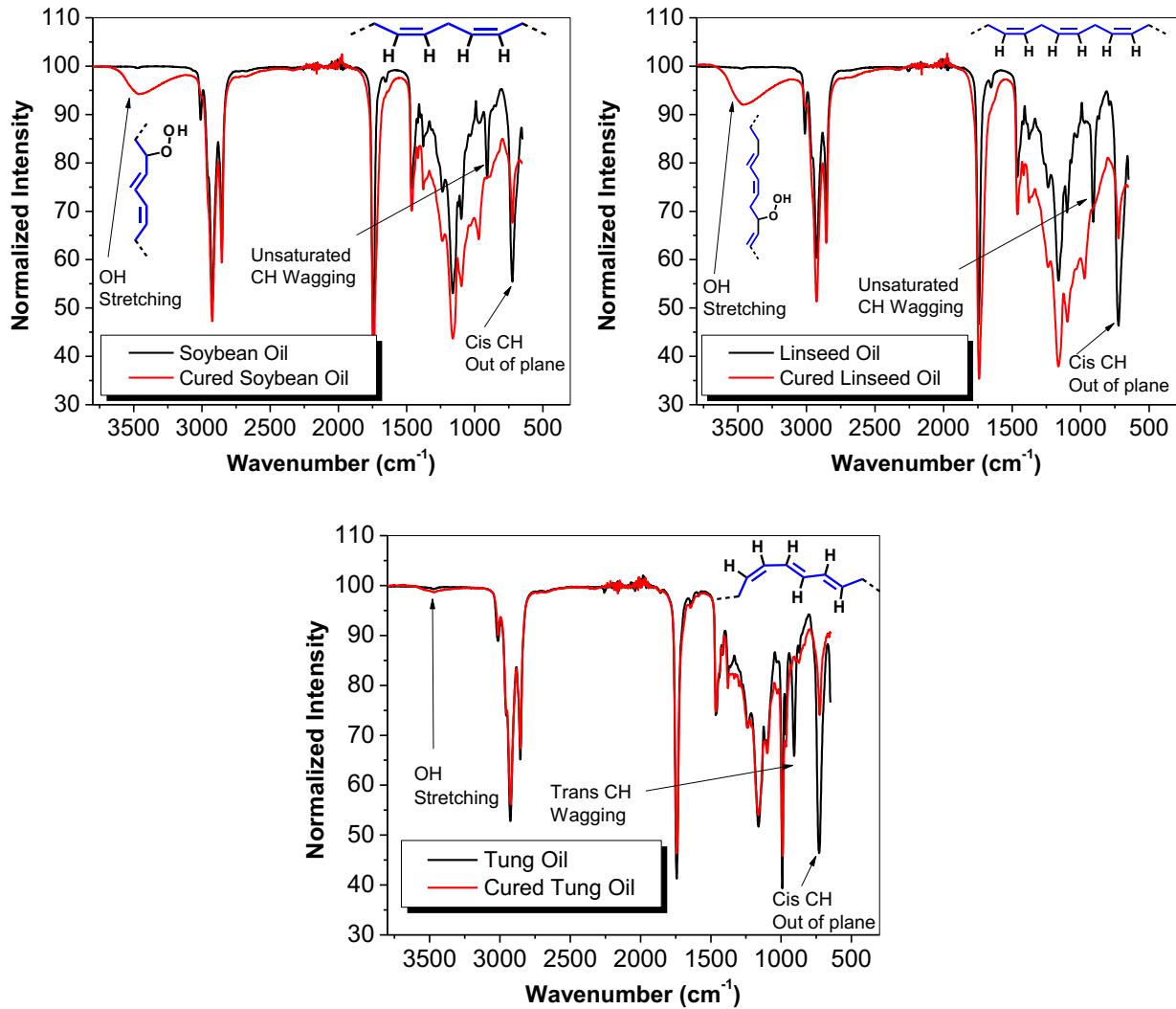


Figure 2. (A) Optical images of cured seed oils in aluminum foils (from left to right: soybean, linseed and tung); (B) FTIR spectra of individual uncured and cured seed oils.

Fourier-transform infrared spectroscopy (FTIR) was used to characterize the curing process of three oils[20]. Both pristine liquid oils and cured solid films were compared, as shown in **Figure 2B**. The most distinct change is closely associated with CH wagging (around 910 cm^{-1}) from unsaturated and conjugated double bonds for all three oils[21, 22]. After the curing, these characteristic absorption peaks almost completely disappeared, while the peaks corresponding to the cis-CH out-of-plane vibration substantially reduced (around 720 cm^{-1}). Such dramatic changes indicated that the curing occurred within the unsaturated bonds. However, there is an evident difference between tung oil and soybean oil as well as linseed oil. After the curing, the latter two oils exhibit strong and broad absorption peaks around $3100\text{-}3650\text{ cm}^{-1}$, possibly attributed to the

formation of hydroxy group or hydroperoxide. However, this peak is largely missing for tung oil. As shown in **Figure 1**, the curing of seed oils undergoes many steps. FTIR results demonstrated that all three oils were cured. The almost absence of hydroxy groups in tung oil indicated that its curing is the most efficient, consistent with the common knowledge.

In addition, the cured seed oil coatings on wood were also characterized by FTIR via attenuated total reflection (ATR), which has been used by many research groups[23, 24]. As shown in **Figure S1** in supplementary information, broad absorption peaks at 3200-3400 cm^{-1} , strong peaks around 2800-3050 cm^{-1} and 1650-1800 cm^{-1} are consistent with cured solid films shown in **Figure 1**. More critically, there are no evident peaks around 700-950 cm^{-1} associated with CH wagging and cis-CH out-of-plane vibration of unsaturated or conjugated double bonds, further validating the successful curing of seed oils on wood.

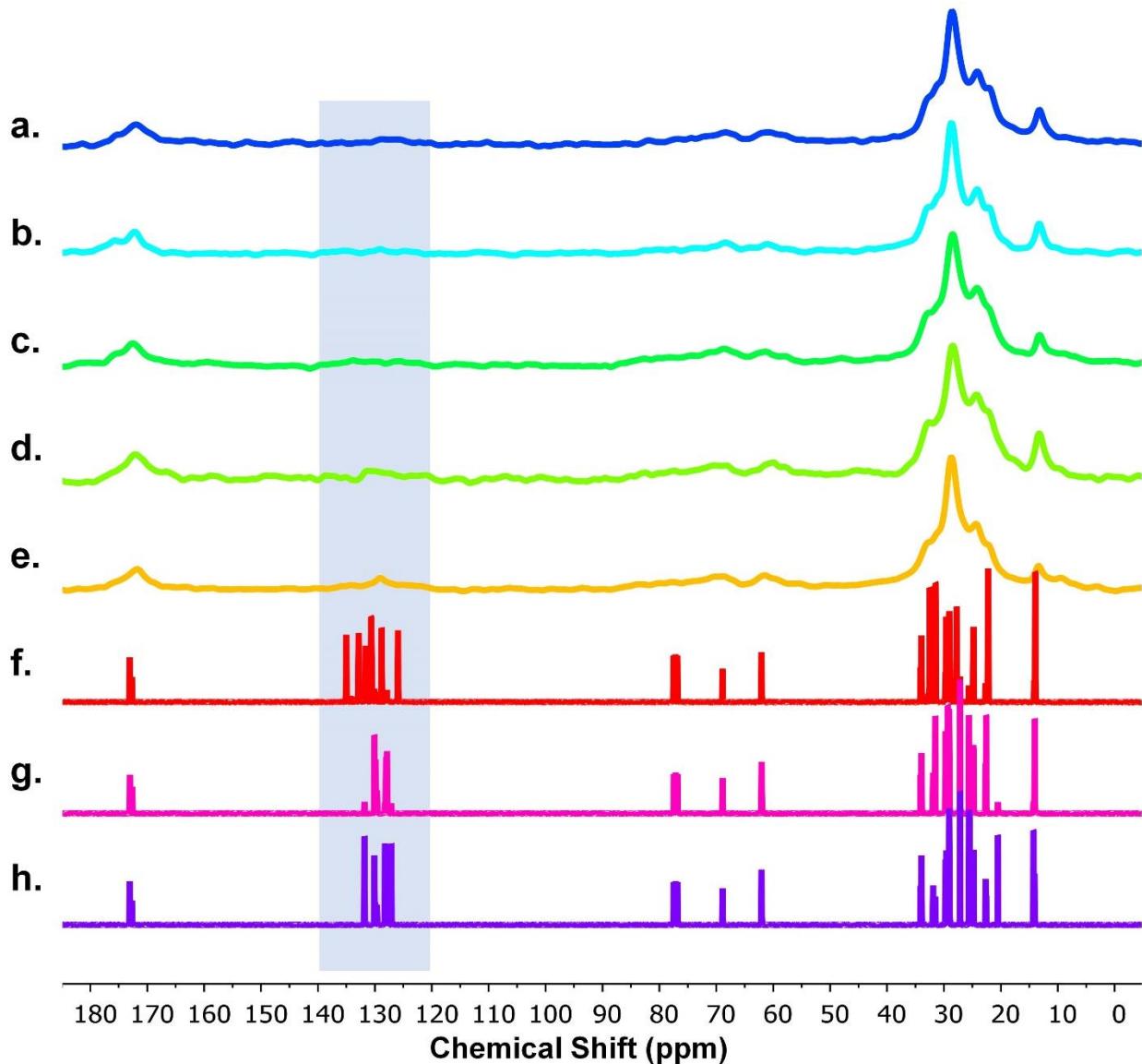


Figure 3. Solid-state ^{13}C NMR spectra of individual uncured and cured seed oils: a. cured tung/soybean oils (2/8 v/v); b. cured soybean oil; c. cured tung/linseed (2/8 v/v); d. cured tung oil; e. cured linseed oil; f. tung oil; g. soybean Oil; h. linseed oil.

The crosslinked, solid cured seed oils were further monitored by solid state ^{13}C NMR spectroscopy, which can characterize the change of unsaturated double bonds because of curing[25-29]. **Figure 3** shows that all three virgin oils (**f**, **g**, **h**) have characteristic peaks at 125-140 ppm and 60-80 ppm, respectively corresponding to the $-\text{C}=\text{C}-$ double bonds and the carbon atoms from the glyceride group. Significant changes are noticeable after the oils are cured. The double bond peaks in the cured individual (**b**, **d**, **e**) or mixed oils (**a**, **c**) largely disappear. Drastic

reduction related to the glyceride carbons indicates that the surrounding structures are also substantially changed. Taken together, the solid-state ^{13}C NMR results demonstrate the efficient crosslinking of oil structures after the curing process, corroborating with the observation by infrared spectroscopy.

3.2. Chemical resistance, hydrophobicity and thermal stability of cured seed oils

Woods are knowingly and willfully chosen to use in indoor and materials such as kitchen floor, bathroom sink, living room wall or outdoor patio because of its natural outlook and vanity [10]. However, constant water absorption and desorption incline to destroy wood's beauty and long-term potency. That's why one of requirements for outdoor and indoor coatings is testing their resistance to chemicals and water[30]. Thus, the cured seed oil solids were evaluated by immersing samples in water, hexane and acetone. Hexane is picked as a well-known apolar organic solvent that susceptible to dissolve oils. As shown in **Figure 4**, all solutions appear clear and colorless after immersion of cured oils for two days, although these solids have a yellowish color. Quantitatively, both swelling and solubility ratios were determined (**Table S1**, supplementary information). The swelling ratio indicates the level of solvents trapped inside the solid, while the solubility ratio demonstrates the fraction of dissolvable oils in the solid. Both water and hexane immersions yield more accurate data, however, in acetone, some cured oils are sticky and hard to take out completely for measurement. Thus, the data lists the results from water and hexane. Both ratios are typically around 10% and lower. These results clearly indicate that the cured seed oils are resistant to water and susceptible organic solvents.

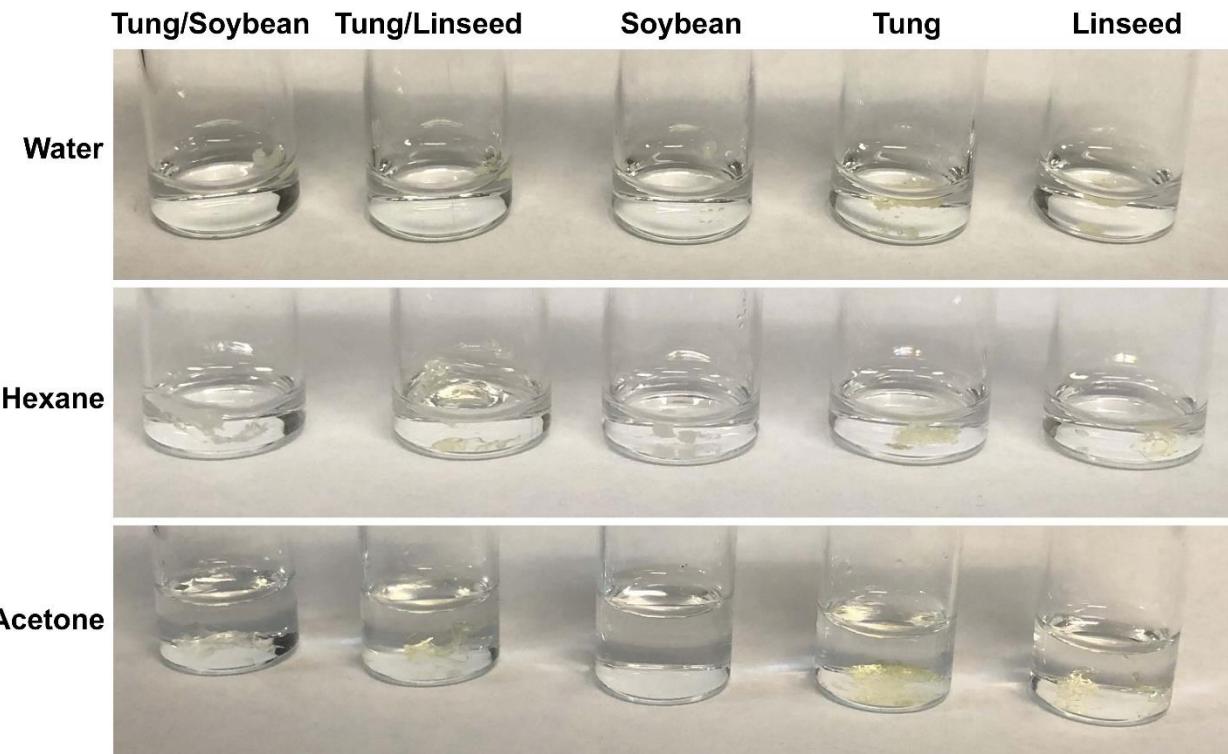


Figure 4. Chemical and water resistance evaluation: optical images of different cured seed oil solids immersed in water, hexane and acetone for two days (for mixed oils Tung/Soybean and Tung/Linseed, the volume ratio is 2/8).

The water resistance was also evaluated by contact angle measurement. Given the hydrocarbon-rich nature of triglycerides, the coatings of seed oils should significantly increase the hydrophobicity of wood surface. Static contact angle images of water droplets on coated wood are shown in **Figure 5**. The pristine maple wood (control) has a contact angle of essentially at 0° with water fully spread out (**Figure S2**). However, contact angles of 101.5° , 107.2° , and 97.8° were observed respectively for cured soybean, tung, and linseed oil coatings, indicating that the coating materials are hydrophobic.

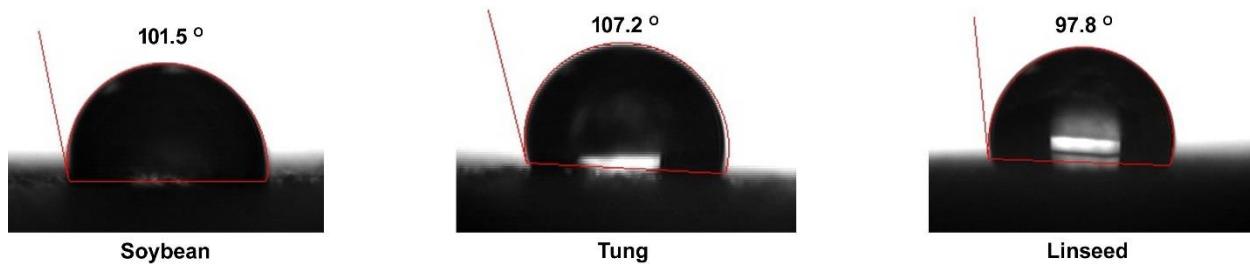


Figure 5. Static water contact angle measurement on seed oil-coating wood surfaces.

On the other hand, thermal stability of cured seeds oils is another important factor for coating applications. In addition to wet areas usage of wood materials, they are potentially exposed extremely hot conditions in both indoor and outdoor. Thermogravimetric analysis (TGA) was carried out for individual oils and mixed oils to determine degradation temperature. The TGA curves in **Figure S3** have similar weigh loss profiles for all five oils (tung, linseed, soybean and tung/linseed (2/8 v/v) and tung/soybean (2/8 v/v) oils). The results indicate that these coating materials are thermally stable, as the onset degradation temperature of 5% weight loss is in the range of 197-225 °C (**Table S2**, supplementary information).

3.3. Inhibition of fungal growth by individual seed oil coating

It is well known that tung oil has been used as water-repellent resins in various applications[31], partially due to its excellent hydrophobicity, which also imparts tung oil being antifouling. Thus, it was hypothesized that tung oil and other seed oils could be antifungal. The successful curing of tung, linseed and soybean oils motivated us to test the inhibition of fungal growth on wood[32, 33]. White-rot fungus was evaluated as it is one of the most commonly fungi to grow on wooden surfaces[34]. White-rot fungus can grow in a wide temperature range, and its optimal growth occurs at 24-32 °C[35], which is close to the same preset temperature for incubators.

To test the efficacy of these coatings, agar plates were first spread with white-rot fungus, then oil-coated wood disks were placed on the surface of each agar plate, and fungal growth was observed. The larger the fraction of growth inhibition area on each plate, the more effective the coating has on its antifungal property. It was further predicted that tung oil would have the best effect in preventing fungal growth on maple wood, followed by linseed, and then soybean oil. The three oils have different chemical compositions based on the number of double or conjugated double bonds in each oil. Therefore, it was hypothesized that the chemical compositions of seed oils would determine the difference in inhibition of fungal growth.

Different from many antimicrobial or antifungal agents, these oil coatings were not observed with the formation of circular inhibition zones, but with the gradual transmission from one area to other areas. Representative growth photos are shown in **Figure 6**. Both the area and thickness of fungal growth depend on the type of oils. On Day 3, a significant area was not occupied by fungal growth for all the oils. In contrast, on Day 4, the plate with control samples was almost full of a thick layer of white rot fungus, while both soybean and linseed oil coatings

exhibited visible inhibition, with only a thinner layer of fungi observed for both. By Day 6, the fungi fully grew on all plates from control, soybean, and linseed oil-coated samples. There was still a difference: the wood disks in control were also covered with fungi, while most disks in latter two samples were still clean. In comparison, tung oil coatings demonstrated substantially better inhibition. Only a small area of fungal growth was observed on Day 6. Full fungal growth did not occur until Day 10.

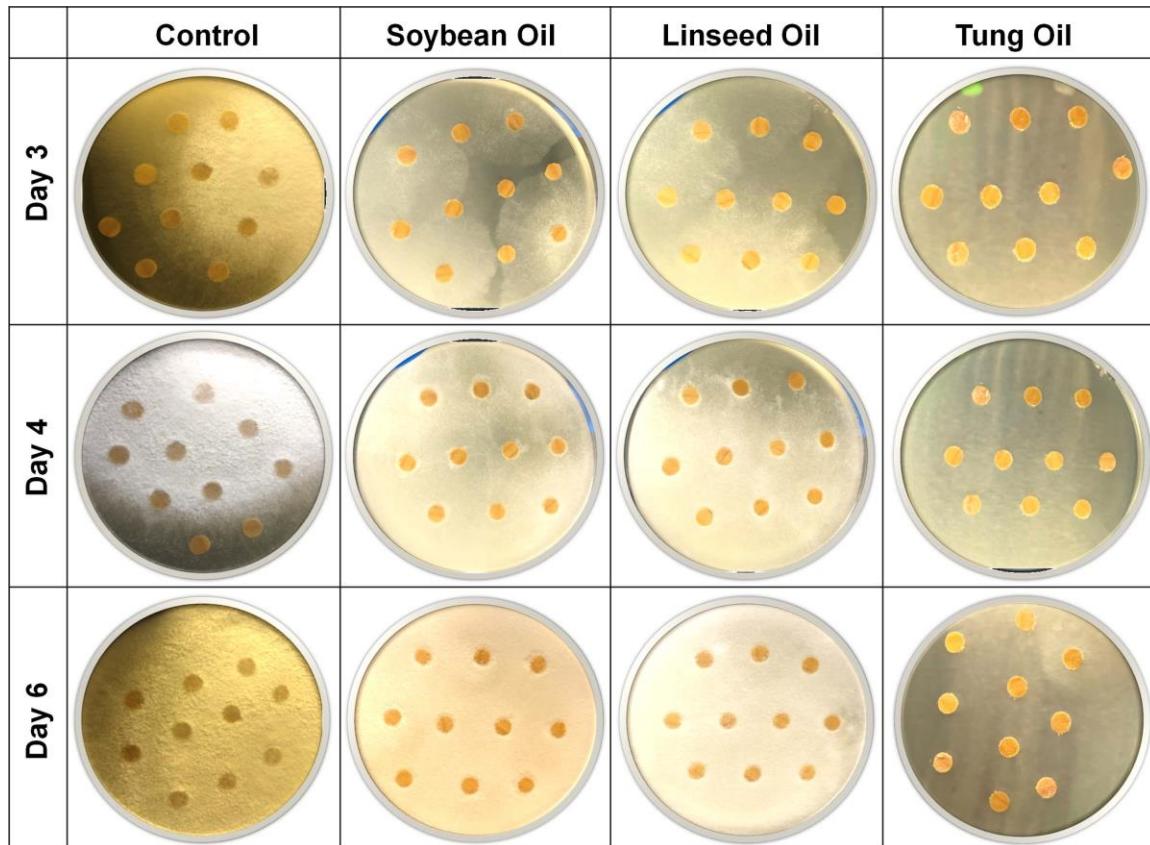


Figure 6. Optical images of time-dependent white-rot fungal growth on agar plates with individual cured oils and the control on maple wood disks.

The inhibition profile of four different types of samples is shown in **Figure 7**. Obviously, tung oil stands out the best. Both soybean and linseeds oils are better than the control but exhibiting a similar trend. These results indicate that individual seed oils could play a limited role as antifungal coatings. Nevertheless, the inhibition growth profiles validated the initial hypothesis that the chemical compositions dictate the antifungal properties.

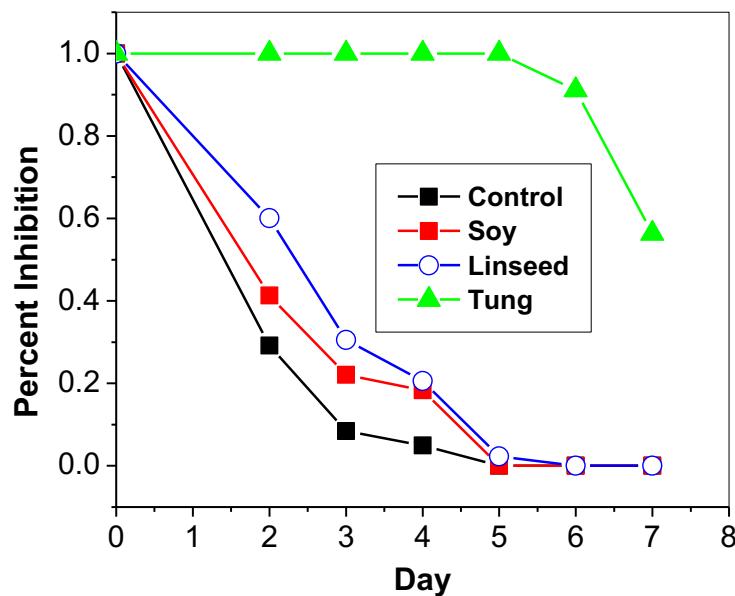


Figure 7. Profiles of inhibition of white-rot fungal growth on agar plates by individual cured oils and the control.

3.4. Curing and fungal inhibition of mixed seed oil coatings on wood

Given the excellent curing and antifungal properties of tung oil, it was further hypothesized that tung oil curing chemistry could enhance the efficiency of linseed and soybean oils, if they are mixed. To test this hypothesis, we mixed 20% tung oil with either 80% linseed or 80% soybean oil volume and then carried out the curing process and evaluated their inhibition against white-rot fungi. The reason we chose 20% tung oil was to keep the dominance of linseed or soybean oils and maintain reasonable presence of tung oil for faster curing.

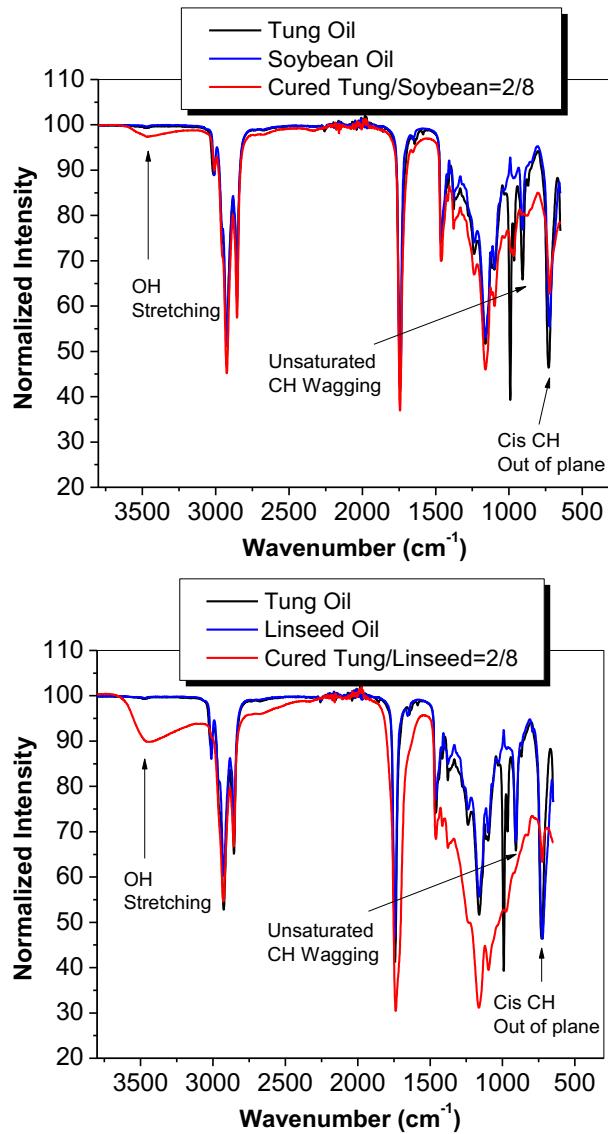


Figure 8. FTIR spectra of individual seed oils and cured mixed seed oils containing 20% (volume) tung oil.

Visually mixed oils were cured significantly faster than individual linseed or soybean oil. It only took about three days for tung/soybean (2/8 in volume) oils to stop flow, compared with one week for soybean oil alone under the same conditions. Within a day, tung/linseed (2/8 in volume) oils solidified. The curing was also monitored by FTIR, as shown in **Figure 8**. In both types of mixed oils, the CH wagging from unsaturated double bonds disappeared with the absorption of the cis-CH out of plane vibration greatly reduced. It was surprising that the OH stretching in mixed tung/soybean (2/8 in volume) oils is substantially weaker than in tung/linseed

(2/8 in volume) oils. It could be related to possible heterogeneity of cured samples. The early solidification may slow down the diffusion of triglyceride molecules of tung oil into those of linseed oil. Thus, some of hydroperoxide groups were not completely crosslinked. Both ATR-FTIR of coatings on wood surface (**Figure S1**) and solid-state ^{13}C NMR (**Figure 3, a and c**) demonstrate the successful curing of mixed oils. In addition, chemical resistance (**Figure 4, Table S1**), and TGA evaluation (**Figure S3** and **Table S2**) indicate that the mixing does not change most properties of oils in any significant manner compared to individual oils.

The inhibition of mixed oil coatings against white-rot fungal growth was further evaluated (**Figure 9**). Overall, the mixed oil coatings are much more effective on inhibition than the control. On Day 4, agar plates with either the tung/soybean or tung/linseed coating only had a small area of fungal growth, while the control samples allowed the significant fungal growth. A complete coverage of fungi took the control samples five days, while it would take more than seven days for tung/soybean and tung/linseed coatings. It was surprising that tung/soybean oil seemed to better inhibit fungal growth than tung/linseed oil, which corroborated with the curing monitored by FTIR. **Figure 10** shows the inhibition profiles of three different types of samples. Though there is a similarity between tung/soybean and tung/linseed coatings, both coatings are appreciably more effective than the control. Compared with the inhibition profile of individual oil coatings in **Figure 7**, the mixing of tung oil indeed validated the hypothesis of enhanced efficacy (at least 50% better in terms of the number of days to achieve a similar level of inhibition) for both soybean and linseed oils.

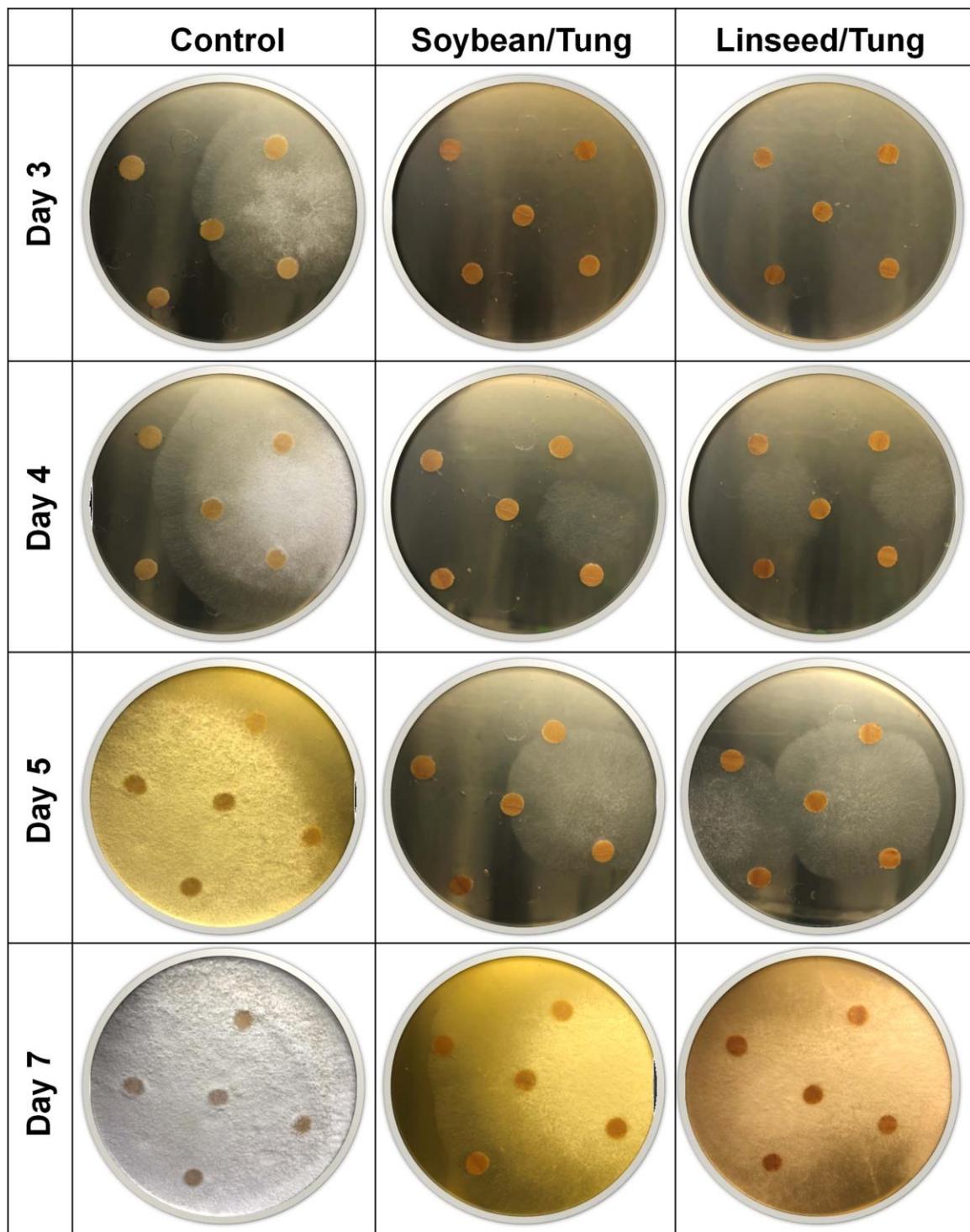


Figure 9. Optical images of white-rot fungal growth on agar plates with mixed cured oils and the control on maple wood disks.

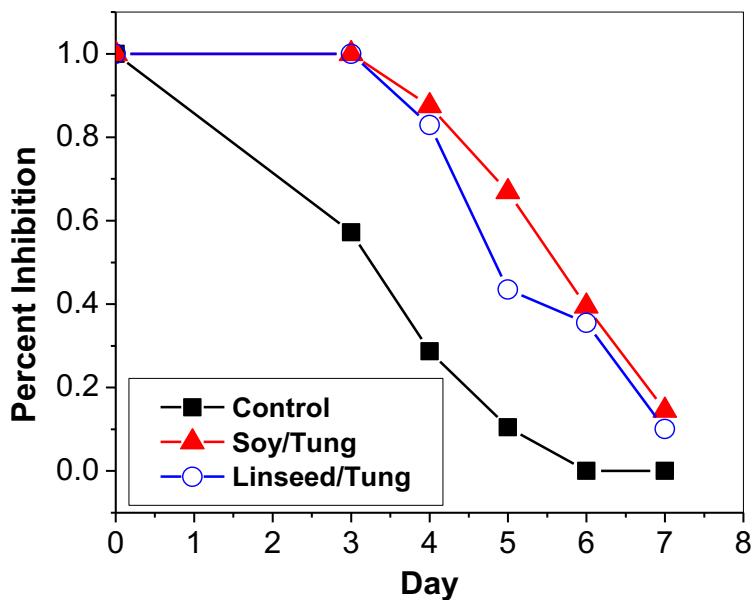


Figure 10. Profiles of inhibition of white-rot fungal growth on agar plates by mixed cured oils and the control.

4. Discussion

Because tung oil is predominantly produced in Asia on a relatively small scale and has a unique chemical composition that no other seed oils possess, the purpose of this study was to explore if more widely available seed oils could be used as effective coatings to prevent fungal growth on wooden surfaces. Linseed oil and particularly soybean oil are abundant but have been much less explored as antifungal coatings. Tung oil is the most effective because it has predominantly conjugated double bonds (>80% alpha-eleostearic acid) that make the oil easier to produce more resonance radicals and to facilitate crosslinking and polymerization, which would lead to the formation of a protective hydrophobic coating against fungal growth[36, 37]. The other oils do not possess conjugated bonds; instead, they have a mixture of saturated, oleic, linoleic, or linolenic fatty acids covalently linked together with much lower double bonds. Thus, the curing is slower with the coating less protective against fungi.

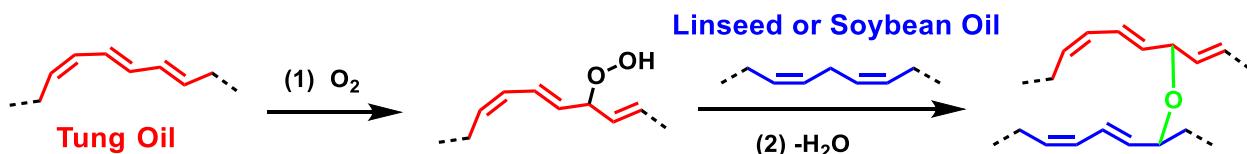


Figure 11. A proposed mechanism of curing chemistry involving mixed cured oils containing tung oil and linseed or soybean oil.

The facile production of resonance radicals and hydroperoxide in tung oil can facilitate the curing of soybean or linseed oil at a faster rate[17, 18], as a proposed chemical crosslinking process is illustrated in **Figure 11**. Linseed contains 53% linolenic acid and soybean contains 58% linoleic acid. Both have a significant fraction of allylic hydrogen for abstraction during the crosslinking. Most likely the reactions start with tung oil through resonance radicals involving conjugated double bonds, which produce active hydroperoxide groups. These active groups could then attack unconjugated double bonds from soybean or linseed oil by homolytic dissociation of the peroxide bond and water condensation. Certainly, the curing process would be largely dictated by the fraction of tung oil in the mixture.

5. Conclusions

In summary, three natural seed oils, tung, linseed, and soybean, were used to prepare VOC-free green coatings and to investigate how oil compositions could inhibit fungal growth on wood. All oils underwent efficient curing processes under direct sunlight, as evidenced by FTIR and NMR spectroscopic studies. The cured oils show high chemical and water resistance and thermal stability. Given the variation in the number and type of unsaturated double bonds, it was hypothesized that the oil compositions would impact the fungal growth on wood, with tung oil being the most efficient inhibitor, followed by linseed oil and soybean oil. The results showed that all oil-based coatings inhibited the white-rot fungal growth. As expected, tung oil was the most effective, with linseed and soybean being less potent. However, further mixing either soybean or linseed oil with a small fraction of tung oil significantly enhanced the curing efficiency (two times faster) and antifungal efficacy (50% better). This approach could open an avenue toward green coatings using abundant and low-cost natural resources as renewable feedstocks.

AUTHOR INFORMATION

Corresponding Author

Jie Li - Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States; orcid.org/0000-0001-7977-6749; Email: LI439@mailbox.sc.edu

Authors

Cathy C. Tang - Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States.

Ying Li - Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States.

Leman Kurnaz - Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States.

Author contributions

Cathy Tang: Conceptualization, Methodology, Investigation, Writing-Original draft preparation. **Ying Li:** Supervision, Investigation. **Leman Kurnaz:** Investigation, Data curation. **Jie Li:** Methodology, Supervision, Writing- Reviewing and Editing

Notes

The authors declare no competing financial interest.

Acknowledgements

We would like to acknowledge Dr. Dan Xue and Dr. Lukuan Hou at University of South Carolina for assistance in the agar diffusion studies. C. Tang acknowledges the Magnet Programs at Spring Valley High School and thanks Dr. Michelle Wyatt and Ms. Lindsey Rega at Spring Valley High School for guidance on developing the research idea. This work is partially funded by a National Science Foundation EPSCoR Program OIA-1655740.

Appendix A. Supplementary data

Supplementary data to this article can be found online at

References

- [1] K.D. Weiss, Paint and coatings: A mature industry in transition, *Prog. Polym. Sci.*, 22 (1997) 203-245.
- [2] J.B. Zimmerman, P.T. Anastas, H.C. Erythropel, W. Leitner, Designing for a green chemistry future, *Science*, 367 (2020) 397-400.
- [3] M.F. Cunningham, J.D. Campbell, Z. Fu, J. Bohling, J.G. Leroux, W. Mabee, T. Robert, Future green chemistry and sustainability needs in polymeric coatings, *Green Chem.*, 21 (2019) 4919-4926.

[4] M. de Meijer, Review on the durability of exterior wood coatings with reduced VOC-content, *Prog. Org. Coat.*, 43 (2001) 217-225.

[5] U.S.G.B. Council, Green Building Rating SystemTM Version 2.0: Leadership in Energy and Environmental Design, in: U.S.G.B. Council (Ed.), 2020.

[6] J.G.H. Hermens, T. Freese, K.J. van den Berg, R. van Gemert, B.L. Feringa, A coating from nature, *Sci. Adv.*, 6 (2020) eabe0026.

[7] J.T.P. Derkxen, F.P. Cuperus, P. Kolster, Paints and coatings from renewable resources, *Ind. Crops Prod.*, 3 (1995) 225-236.

[8] L.D. Chambers, K.R. Stokes, F.C. Walsh, R.J.K. Wood, Modern approaches to marine antifouling coatings, *Surf. Coat. Technol.*, 201 (2006) 3642-3652.

[9] C. Maduka, N.C. Igwilo, Microorganisms Survive In Paints, *Curr. Anal. Biotechnol.*, 2 (2019) 1-5.

[10] J. Miklečić, V. Jirouš-Rajković, Effectiveness of finishes in protecting wood from liquid water and water vapor, *J. Build. Eng.*, 43 (2021) 102621.

[11] U. Poth, Drying Oils and Related Products, in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCh, Weinheim, 2001.

[12] O. Schmidt, Wood and tree fungi: Biology, Damage, Protection, and Use, Springer, Heidelberg, 2006.

[13] J. Greenfield, Tung oil, *J. Am. Oil Chem. Soc.*, 36 (1959) 565-574.

[14] A. Redfield, B. Ketchum, Marine fouling and its prevention, Woods Hole Oceanographic Institution, (1952).

[15] S.Z. Erhan, Industrial uses of vegetable oil, AOCS publishing, New York, 2005.

[16] M. Bockisch, Fats and oils handbook, AOCS Press, Urbana IL, 2015.

[17] E. Choe, D.B. Min, Mechanisms and factors for edible oil oxidation, *Compr. Rev. Food Sci. Food Saf.*, 5 (2006) 169-186.

[18] Y. Gan, X. Jiang, Photo-cured materials from vegetable oils, in: Z. Liu, G. Kraus (Eds.) Green Materials from Plant Oils, Royal Society of Chemistry, Cambridge, 2014, pp. 1-27.

[19] A. Köckritz, A. Martin, Oxidation of unsaturated fatty acid derivatives and vegetable oils, *Eur. J. Lipid Sci. Technol.*, 110 (2008) 812-824.

[20] J. Mallégol, J.-L. Gardette, J. Lemaire, Long-term behavior of oil-based varnishes and paints I. Spectroscopic analysis of curing drying oils, *J. Am. Oil Chem. Soc.*, 76 (1999) 967-976.

[21] L. De Viguerie, P. Payard, E. Portero, P. Walter, M. Cotte, The drying of linseed oil investigated by Fourier transform infrared spectroscopy: Historical recipes and influence of lead compounds, *Prog. Org. Coat.*, 93 (2016) 46-60.

[22] A. Schönemann, H.G. Edwards, Raman and FTIR microspectroscopic study of the alteration of Chinese tung oil and related drying oils during ageing, *Anal. Bioanal. Chem.*, 400 (2011) 1173-1180.

[23] Z. He, H.N. Cheng, S. Nam, Comparison of the wood bonding performance of water- and alkali-soluble cottonseed protein fractions, *J. Adhes. Sci. Technol.*, 35 (2021) 1500-1517.

[24] Z. He, J. Qian, L. Qu, N. Yan, S. Yi, Effects of Tung oil treatment on wood hygroscopicity, dimensional stability and thermostability, *Ind. Crops Prod.*, 140 (2019) 111647.

[25] T.M. Lacerda, A. Gandini, The cationic polymerization of tung oil and its fatty-acid methyl ester, *Ind. Crops Prod.*, 157 (2020) 112886.

[26] Z. Liu, S.Z. Erhan, Ring-Opening Polymerization of Epoxidized Soybean Oil, *J. Am. Oil Chem. Soc.*, 87 (2010) 437-444.

[27] G.L. Marshall, The analysis of cured drying oils by swollen state ^{13}C -NMR spectroscopy, *Eur. Polym. J.*, 22 (1986) 231-241.

[28] J. Li, S. Pradyawong, Z. He, X.S. Sun, D. Wang, H.N. Cheng, J. Zhong, Assessment and application of phosphorus/calcium-cottonseed protein adhesive for plywood production, *J. Clean. Prod.*, 229 (2019) 454-462.

[29] J. Li, S. Pradyawong, X.S. Sun, D. Wang, Z. He, J. Zhong, H.N. Cheng, Improving adhesion performance of cottonseed protein by the synergy of phosphoric acid and water soluble calcium salts, *Int. J. Adhes. Adhes.*, 108 (2021) 102867.

[30] R.C. Larock, X. Dong, S. Chung, C.K. Reddy, L.E. Ehlers, Preparation of conjugated soybean oil and other natural oils and fatty acids by homogeneous transition metal catalysis, *J. Am. Oil Chem. Soc.*, 78 (2001) 447-453.

[31] K. Brown, W. Keeler, The history of tung oil, *Wildland weeds*, 9 (2005) 4-24.

[32] R. Stirling, A. Temiz, Fungicides and insecticides used in wood preservation, in: T.P. Schultz, B. Goodell, D.D. Nicholas (Eds.) *Deterioration and Protection of Sustainable Biomaterials*, ACS Publications, Washington DC, 2014, pp. 185-201.

[33] T. Ravikumar, H. Murata, R.R. Koepsel, A.J. Russell, Surface-active antifungal polyquaternary amine, *Biomacromolecules*, 7 (2006) 2762-2769.

[34] G. Daniel, Fungal and bacterial biodegradation: white rots, brown rots, soft rots, and bacteria, in: T.P. Schultz, B. Goodell, D.D. Nicholas (Eds.) *Deterioration and protection of sustainable biomaterials*, ACS Publications, Washington DC, 2014, pp. 23-58.

[35] B. Goodell, J.E. Winandy, J.J. Morrell, *Fungal Degradation of Wood: Emerging Data, New Insights and Changing Perceptions, Coatings*, 10 (2020) 1210.

[36] E. Almeida, T.C. Diamantino, O. de Sousa, Marine paints: The particular case of antifouling paints, *Prog. Org. Coat.*, 59 (2007) 2-20.

[37] Z. He, D.C. Chapital, H.N. Cheng, K. Thomas Klasson, O.M. Olanya, J. Uknalis, Application of tung oil to improve adhesion strength and water resistance of cottonseed meal and protein adhesives on maple veneer, *Ind. Crops Prod.*, 61 (2014) 398-402.