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Section 4 **Processes and properties**

The use of new, aqueous chemical wood modifications to improve the durability of wood-plastic composites

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The use of new, aqueous chemical wood modifications to improve the durability of wood-plastic composites

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ABSTRACT

The wood flour used in wood-plastic composites (WPCs) can biologically deteriorate and thus the overall mechanical performance of WPCs decrease when exposed to moisture and fungal decay. Protecting the wood flour by chemical modification can improve the durability of the wood in a nontoxic way so it is not harmful to the environment. WPCs were made with modified wood flour and then evaluated for moisture sorption, fungal resistance and mechanical performance. Two different chemical modifications at 2 different levels were used: organosilicate (OS, 1% and 2.5%) and cobalt sulfate (CoS, 2.5% and 5%). All modifications had less weight loss than the unmodified controls with the 2.5% OS blend showing no weight loss from decay by either brown or white rot fungi. Water soaking for 1-week at elevated temperature (70°C) was more aggressive for laboratory decay and mechanical testing as shown by higher weight loss and lower mechanical properties compared to 2-week water soaking at room temperature (23°C). Moisture exposure decreased the mechanical properties, but 2.5% OS, 2.5% CoS and 5% CoS had better performance than the unmodified controls and 1% OS after 70°C conditioning and decay.

Keywords: WPC, organosilicate, cobalt (II), fungal decay, moisture, mechanical properties

1. INTRODUCTION

When untreated nondurable wood species are exposed to adverse environments they deteriorate due to moisture, weathering and biological decay. The most common way of protecting the wood is with toxic preservatives but with concerns over human and environmental health, the use of chemical modification for wood protection is increasing throughout the world.

A literature review found that cobalt(II) complexes including cobalt(II) carboxylates (Suran, Vodova et al. 1987), cobalt(II) hexanoate (Hirata 2004), and cobalt(II) azaconazole (Yang, Xie et al. 2009) were used for fungal decay protection, and cobalt(II) complexes of fatty amines (West 2004) and cobalt(II) octanoate (Voinscu and Dulgheriu 2005) were used for UV protection. In preliminary studies, we found that cobalt (II) sulfate bonded to solid wood was highly effective against both brown and white rot fungi below 1% concentration and that it was resistant to water leaching. Cobalt (II) does not change the color of the solid wood making it more acceptable to consumers.

A literature review of organosilicates found only one (Siloxane) (Vasilevskaya, Krotikov et al. 1977) was used as a water repellent for wood coatings. There were no reports using organosilicates for fungal and termite decay protection in wood products. In our preliminary investigations with solid wood, we found that an organosilicate prepared from sodium silicate and a quaternary amine was effective against a brown and white rot fungus at 1% solution

concentration even after water leaching daily for two weeks. Based on our initial investigation the mechanism of decay protection of organosilicates may be based on toxicity or may resemble that of surfactants that disrupt the fungal membrane's semi-permeability, making it more acceptable to the environment. As a result, organosilicates have the potential of becoming the alternative to heavy metal free wood preservatives. Organosilicates can be synthesized from inexpensive sodium silicate (water glass) and environmentally-friendly, industrial organic compounds in a short time with a high yield (90%). Organosilicates are neutral compounds, insoluble in water and stable for a long time in the formulated aqueous systems.

The wood protection systems in this study are intended to chemically modify the wood by bonding directly to the wood with the goal of providing non-toxic methods of wood protection not only for fungal resistance but UV resistance as well. The objective was to modify wood flour with either cobalt (II) sulfate or an organosilicate, produce WPCs with 50% modified wood flour and 50% HDPE by injection molding, and then run laboratory evaluation of WPCs for moisture and biological resistance, as well as mechanical properties.

2. EXPERIMENTAL METHODS AND MATERIALS

The plastic was an injection molding grade of high density polyethylene (HDPE) with a melt flow index of approximately 5 g/10 minutes at 190°C and 2.16 kg (grade HD 6605.70, Exxon Mobil Chemical, Spring, Texas). The filler was nominal 40-mesh western pine wood flour (grade 4020) from American Wood Fibers (Schofield, Wisconsin). The cobalt (II) sulfate heptahydrate and the chemicals to make organosilicate were from Sigma-Aldrich Chemical (Milwaukee, Wisconsin).

2.1 Chemical synthesis and wood flour modifications

Synthesis of organosilicate: Didecyl dimethyl ammonium chloride (DDA, 50% solution, 134.55 g, Fw: 362.97, 185.7 mmoles) dissolved in distilled water (300 ml) was stirred into sodium silicate (30% solution, 150 g. Fw: 242.23, 185.7 mmoles) portion wide (50 to 100 ml) over 30 minutes at room temperature. After adding the remaining DDA (100 ml), a white solid organosilicate precipitate appeared. The organosilicate was recovered by filtration and then distilled water added (1 L) and stood for 24 hrs at room temperature. The yield of organosilicate was 93.92 g (83.7%).

Organosilicate wood modification: Wood flour was impregnated with an aqueous basic solution of organosilicate (1.0% or 2.5%) and 3% sodium hydroxide at room temperature. After a 24 hours soak, the solution was neutralized with 1 M hydrochloric acid for 24 hours. The reacted wood flour was filtered, washed with distilled water, air dried for 2 weeks, and then conditioned in a 26.7°C/30% relative humidity room until WPC processing.

Cobalt (II) sulfate wood modification: Wood flour was reacted with two different levels of aqueous cobalt (II) sulfate heptahydrate (2.5% and 5%) and 2% sulfuric acid solutions at 70°C for 24 hours. After the reaction, distilled water was added and soaked for 5 days. The reacted wood flour was filtered, washed with distilled water, air dried for 2 weeks, and then conditioned in a 26.7°C/30% relative humidity room until WPC processing.

2.2 Specimen preparation

The wood flour was compounded with the HDPE in a 1-L high-intensity thermokinetic mixer (K Mixer, Synergistics, Inc., St. Remi de Napierville, Quebec). The thermokinetic mixer is a simple batch mixer in which several high-speed blades supply the energy to melt the polymer and blend

the material. An infrared sensor monitored the material temperature. Batches of 80 g each of HDPE and wood flour were processed at 5,500 rpm (rotor tip speed of about 30 m/sec.) with a discharge temperature of 170°C and a batch time of about 1 min. After the blended material was discharged, it was cold-pressed, granulated, and dried for a minimum of 4 hours at 105°C.

The compounds were molded using a combination microcompounder/microinjection molder (DSM Xplore system, DSM Research, Geleen, Netherlands). The compounder barrel temperatures were set at 190°C and the screw speed was 50 RPMs. A nitrogen blanket was used to minimize degradation. The material was transferred to the injection molder and flexural specimens were molded at 190°C at 13 bars of pressure for 10 seconds. The mold temperature was 20°C. The molded specimen size was 3 x 13 x 127 mm which were then cut to 89 mm in length for evaluations.

2.3 Moisture and fungal exposure

Soil block culture testing was conducted on WPC specimens according to AWPA E10 (AWPA 2013) using both brown rot (*Gloeophyllum trabeum*) and white rot (*Trametes versicolor*) fungi, except that the soil bottles were turned on their side to allow the 89-mm specimen length to fit into a standard soil bottle. Before exposure to fungi, the specimens were conditioned by either water soaking at room temperature (RT, 23°C) for 2 weeks (S) or water soaking at elevated temperature (70°C) for 1 week (S70). Specimens from each formulation were divided into six groups (5 replicates each group), conditioned, weighed, steam sterilized, inserted into horizontal bottles, and then exposed either with or without fungi for 12 weeks at the following conditions:

1. Conditioning by water soak at 23°C (S) for 2 weeks, no fungal exposure (NF)
2. Conditioning by water soak at 23°C for 2 weeks, brown rot fungal exposure (BR)
3. Conditioning by water soak at 23°C for 2 weeks, white rot fungal exposure (WR)
4. Conditioning by water soak at 70°C for 1 week (S70), no fungal exposure
5. Conditioning by water soak at 70°C for 1 week, brown rot fungal exposure
6. Conditioning by water soak at 70°C for 1 week, white rot fungal exposure

After 12 weeks of exposure, the specimens were cleaned of fungal mycelium, weighed, oven dried at 105°C for 48 hours, and then weighed again using an Ohaus Explorer Pro balance (Florham Park, New Jersey), with 0.001-g accuracy. The weight of individual specimens was approximately 4 g. Moisture content and weight loss before and after exposure were calculated along with the average standard deviations based on 5 replicates. Specimens were then tested for flexural properties as described below.

2.4 Mechanical performance

Four-point flexural tests were performed according to ASTM D790–84 (ASTM 1990) on oven-dried specimens to determine the effects of moisture and decay on mechanical properties. The specimen size (3 x 13 x 89 mm) conformed to span and depth requirements of flexural test method ASTM D 790-84. Initial tangent modulus and maximum stress were determined before and after conditioning and on specimens that were removed after 12 weeks exposure and oven-dried at 105ºC. In all cases, failure occurred between the load points in the center third of the specimen.

3. RESULTS AND DISCUSSION

3.1 Moisture and fungal exposure

Table 1 shows the percentage weight losses of the WPCs after conditioning and/or exposure in a 12 week soil block test with and without fungi. Overall the weight losses were low, which is to be expected with injection molded specimens (Clemons and Ibach 2004). The weight losses are

reported on the total composite weight which contains only 50% wood flour. Therefore, the wood weight loss is twice the numbers presented in Table 1. The unmodified solid wood controls had 42% weight loss from brown rot fungi with pine sapwood and 55% weight loss from white rot with sweet gum, which shows that the test fungi were viable.

The unmodified WPC controls had the highest weight losses compared to the WPCs made with chemically modified wood flour. The elevated conditioning at 70°C for 1 week had higher weight loss for both brown rot (4.97%) and white rot (3.08%) fungi, compared to the room temperature 2 week water soak brown rot (2.35%) and white rot (0.81%) fungus.

Table 1: Weight loss of WPC specimens after preconditioning and/or a 12 week soil bottle exposure.

		Weight loss [%]		
Formulation	**Conditioning**	**No fungus**	**Brown rot**	**White rot**
Control-S [a]	0.30 ± 0.01	0.53 ± 0.13	2.35 ± 0.35	0.81 ± 0.19
Control-S70 [b]	1.30 ± 0.05	1.35 ± 0.04	4.97 ± 0.63	3.08 ± 0.63
1% OS-S [c]	0.79 ± 0.06	0.58 ± 0.11	0.81 ± 0.16	0.55 ± 0.15
1% OS-S70	1.50 ± 0.02	1.44 ± 0.04	1.76 ± 0.30	1.30 ± 0.04
2.5% OS-S	0.61 ± 0.03	0.49 ± 0.01	0.35 ± 0.06	0.39 ± 0.04
2.5% OS-S70	1.03 ± 0.02	0.95 ± 0.04	0.76 ± 0.04	0.78 ± 0.02
2.5% CoS-S [d]	0.33 ± 0.03	0.05 ± 0.07	0.77 ± 0.03	-0.06 ± 0.04
2.5% CoS-S70	0.80 ± 0.03	0.58 ± 0.05	1.95 ± 0.21	0.47 ± 0.07
5% CoS-S	0.37 ± 0.02	0.32 ± 0.04	1.22 ± 0.17	0.55 ± 0.10
5% CoS-S70	0.90 ± 0.05	0.65 ± 0.03	1.62 ± 0.28	0.87 ± 0.09

[a]S=2 week water soak at 23°C, [b]S70=1 week water soak at 70°C, [c]OS=organosilicate, [d]CoS=cobalt (II) sulfate

The weight loss from the no fungus soil bottles was subtracted from the total weight loss, resulting in the weight loss just from the decay (Fig. 1). The organosilicate modifications show no decay at the 2.5% OS levels after conditioning at either 23°C or 70°C. The 1% OS showed no decay with white rot and negligible loss with brown rot fungi. The cobalt sulfate modifications showed less weight loss than the controls, but more than the OS. The CoS showed resistance to the white rot and less than 1.5% weight loss from brown rot fungi.

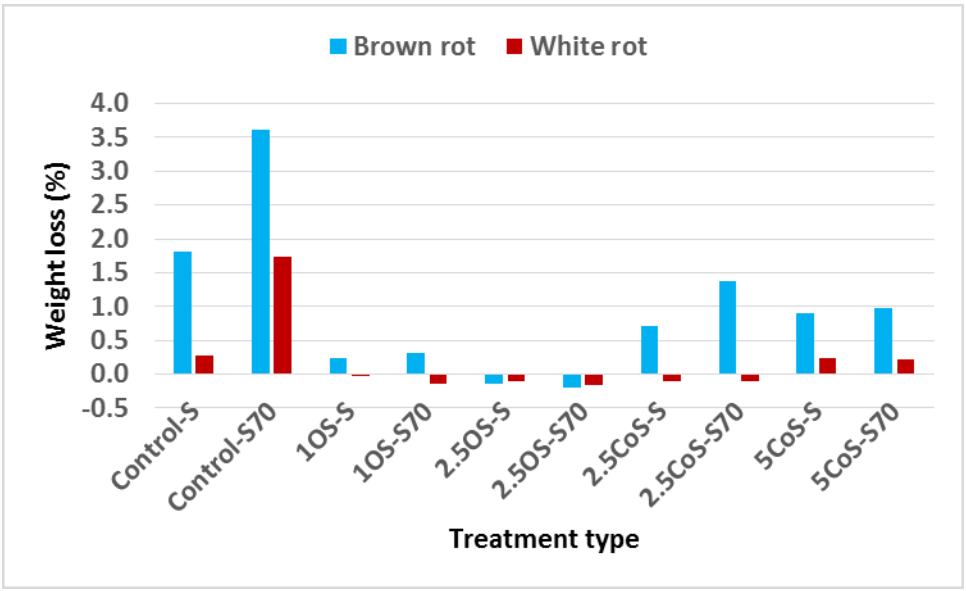

Figure 1. Percentage weight loss from decay

3.2 Mechanical performance

While weight loss due to decay is easily determined, its effect on mechanical performance is more problematic. In addition to fungal decay, factors such as moisture and the chemical treatment itself can influence mechanical performance. For example, Fig. 2 shows the effect of moisture alone on the flexural modulus for all of the formulations. The modulus decreased first with water soaking for 2 weeks at RT (23°C) and then decreased further after 12 weeks in the soil bottles, even when exposed only to moisture and not fungus. Moduli were lower when conditioned by the elevated temperature (70°C) regimen rather than at RT. The modified wood flour WPCs followed this same trend, with some exceptions. The moduli for the 2.5% OS, 2.5%CoS, and 5% CoS formulations were generally higher compared to similar unmodified controls, although some of the trends between them were slightly different. This indicates that both moisture and treatment type affect modulus and must be considered when evaluating the soil bottle data. Although not shown in this paper, the max. stress data followed the same trends as the modulus data.

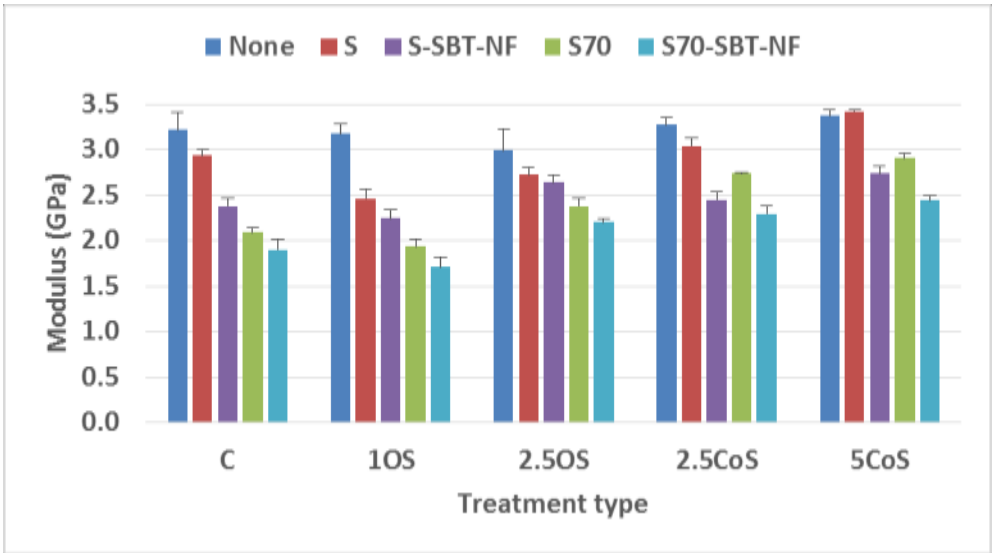

Figure 2. The effect of moisture on the mechanical performance (modulus)

The effects on the modulus from water soaking of the WPCs at room temperature for 2 weeks, and then exposing them to fungi in the soil block test are shown in Fig. 3. In general, the specimens at high treatment levels maintained more of their modulus after exposure to moisture and fungi. Some specimens (e.g., 2.5% OS and 5% CoS-WR) actually showed less reduction in modulus when exposed to fungi. Similar trends were also found in the max. stress data (not shown) and might reflect some variability in the moisture contents of the specimens. Similar findings were also found in tests on specimens conditioned at higher temperature, albeit at lower overall modulus values due to the more severe conditioning (Fig. 4).

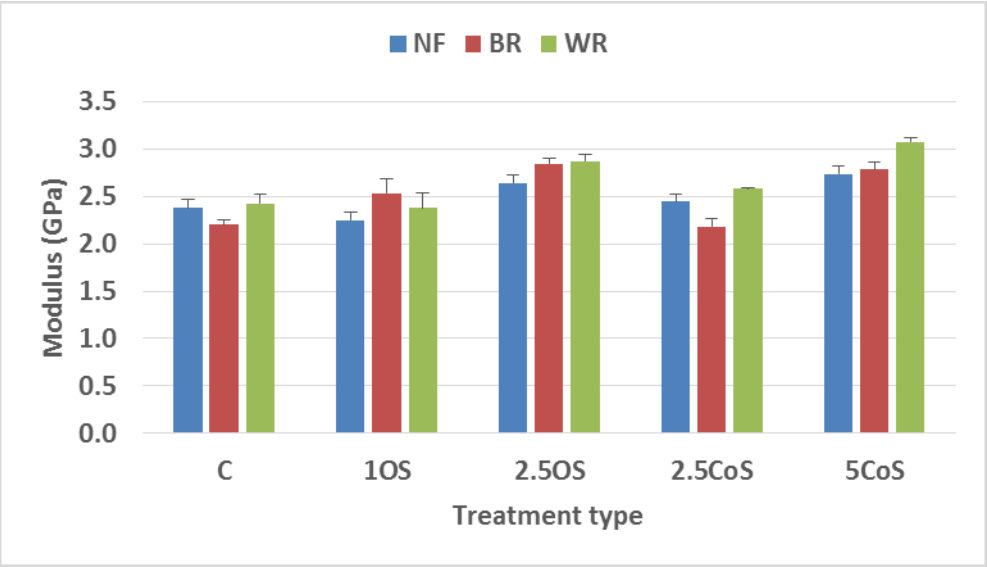

Figure 3. The effect of water soak at 23°C and then 12 week exposure in soil bottles with no fungi (NF), brown rot fungi (BR), or white rot fungi (WR) on the mechanical performance (modulus)

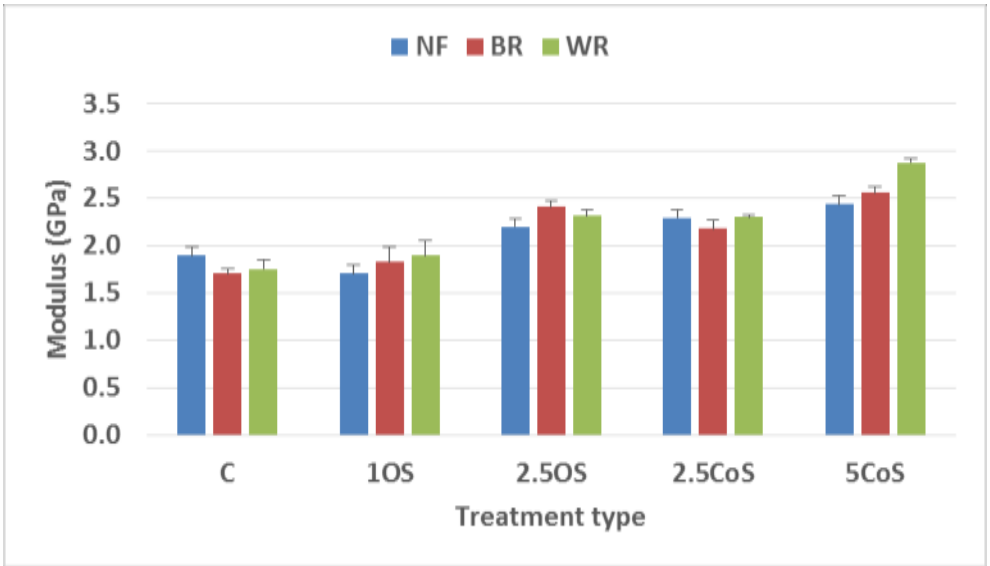

Figure 4. The effect of elevated water soak at 70°C and then 12 week exposure in soil bottles with no fungi (NF), brown rot fungi (BR), or white rot fungi (WR) on the mechanical performance (modulus)

In order to sort out the various effects for chemical treatment, conditioning, and exposure to fungi and further moisture during soil block testing, the loss in modulus was plotted against the moisture content after the soil block test (Fig. 5). The blue circles represent all those WPC specimens that had less than 0.5% weight loss from decay (including no-fungal controls) and whose modulus reductions presumably are nearly entirely due to moisture-related effects, which in turn are affected by chemical treatment and conditioning regimens, for example. A trend line is included for this data. As the WPC moisture content rises above 12.5% (or 25% wood moisture content), there is an exponential increase in the modulus loss. The red squares represent those specimens with greater than 0.5% weight loss from decay. These lay above the trend line, indicating that decay causes additional modulus loss beyond that due to moisture, even at weight losses as little as 0.5%. The weight losses occur when the moisture was in the 10-12% MC range

(20-24% wood MC). As the weight loss from decay increases, so does the loss in modulus, even though the moisture content stays around 10-12%. Those specimens near the high moisture content end of the trend line (i.e. high moisture content yet little or no weight loss) were specimens that were conditioned at elevated temperature and were either in soil bottles without fungus or were treated with organosilicate. The latter suggests a possible fungal resistance mechanism other than just lowering the moisture content, although further investigation is needed.

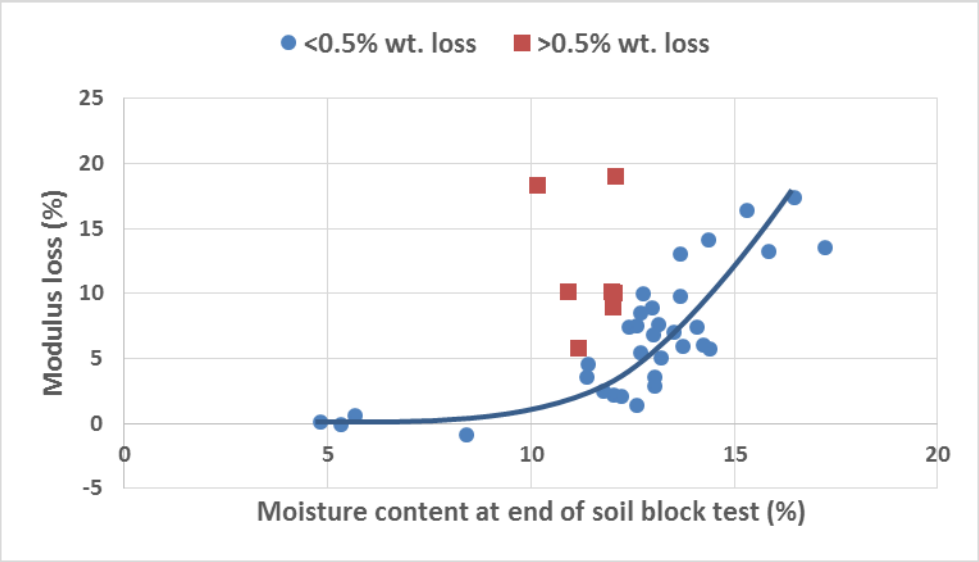

Figure 5. The effect of only moisture vs. moisture and decay on the loss in modulus of WPCs

4. CONCLUSIONS

- The WPCs made with 2.5% OS modified wood flour had the best decay resistance against brown and white rot fungi with either conditioning at 23°C or 70°C.
- The WPCs made with CoS modified wood flour had good resistance to white rot and some resistance against brown rot fungi compared to the controls.
- Moisture alone had a big impact on the mechanical property losses of the WPCs.
- The 2.5% OS, 2.5% CoS, and the 5% CoS had better mechanical performance than the unmodified controls and 1% OS.
- Loss in WPC mechanical properties was sensitive to decay, even as low as 0.5% weight loss.
- Both modifications show effectiveness, but further study is needed on the mechanism.

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