Materials Research. 2019; 22(suppl. 1): e20190045
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2019-0045

Evaluation of a Metal-Organic Composite (Tungsten-Lignin) for Attenuation of Gamma Radiation

Armando Cirilo de Souza[a]*, *Francisco Carlos Cione*[b], *Aline Cardoso da Silva*[c], *Adriana de Fátima Gomes Gouvêa*[c], *Noé Gabriel Pinheiro Machado*[b], *Marcus Paulo Raele*[b], *Jesualdo Luiz Rossi*[b]

[a]*Departamento de Física - CEPEMAT, Universidade Estadual de Mato Grosso do Sul - UEMS, Dourados, MS, Brasil*
[b]*Instituto de Pesquisas Energéticas e Nucleares - IPEN, São Paulo, SP, Brasil*
[c]*Departamento de Engenharia Florestal, Universidade Estadual de Mato Grosso do Sul - UEMS, Aquidauana, MS, Brasil*

Received: January 21, 2019; Revised: June 25, 2019; Accepted: June 29, 2019

The objective of this work was to use tungsten and lignin as precursors to obtain a metal-organic composite tungsten-lignin (W-Lig) using different sintering temperatures. Tungsten is a refractory metal and it was selected for the composite since it is widely used for high-energy radiation shielding as it has an excellent absorption cross section for thermal neutrons. Lignin extracted from lignocelluloses biomass and it was selected to be the organic precursor for the composite due to its multiple applications. Analysis of the composite was performed after sintering processes, using a 3D optical surface profiler and measurement of the gamma radiation attenuation coefficient using cobalt source (Co-60). Metal-organic composites in ratios of W2.5%Lig and W5%Lig (in mass % of lignin) were used. The gradient of the attenuation coefficient differed when standard tungsten and the composites of W2.5%Lig and W5%Lig were compared. Therefore, the attenuation coefficient between unobstructed free radiation and the W5%Lig 90 ºC composite showed a gradient of about 43% in the two characteristic Co-60 energy peaks, with a sample thickness of 0.679 cm the calculated linear attenuation coefficient was 0.832 cm^{-1}.

Keywords: *tungsten, lignin, metal-organic composites, gamma radiation.*

1. Introduction

Numerous materials are of interest as possible components of new composites due to their wide application in various sectors such as transportation, civil construction, automotive, naval, aerospace and nuclear. The pulp industry is a significant contributor to the world economy and has shown interest in research and technological development aimed at refining the waste produced by the process of extracting the cellulose fibers contained in the lignin matrix[1-2]. Tungsten is a refractory metal and was chosen to be combined with lignin due to its extensive physical and mechanical properties including mechanical strength, high melting point, and excellent absorption cross section for thermal neutrons (e.g., tungsten is widely used for shielding from high energy radiation)[3-4].

The lignin is extracted from the lignocellulosic biomass and it was the organic precursor chosen to be used in the samples due to its utility in different types of compounds such as the production of aromatics, adhesives, and as substitute for phenolic resin[5-6]. The objective of this work was to obtain a polymer matrix composite using lignin and a metal as filler, the tungsten powder, in the ratios of W5%Lig and W2.5%Lig (in mass% of lignin) at different sintering temperatures and to analyze the gamma radiation attenuation coefficient. This may contribute directly in the minimization environmental impact considering that lignin is a residue of cellulose[7-8]. The techniques used were, 3D analysis optical profilometry and measurements of the attenuation coefficients of gamma radiation using a cobalt source (Co-60)[9].

However, during the interaction of the ionizing radiation with the samples, the degradation process can occur in the kraft lignin, where the bonds of the carbonyl groups suffer considerable ruptures, leading to the production of monoxide and carbon dioxide in high amounts[10-11]. Nevertheless, the process of lignin degradation and the maximum absorbed dose were not evaluated in the present work, that there was no oxidative degradation, since the source of Co-60 used to measure the linear attenuation coefficient presented low activity, in the order of 35 μCi and the exposure time was 30 minutes. According to Ponomarev[12] and Sun[13], the degradation of cellulose and lignin occurs after an absorption dose in the order of 11 kGy.

Thus, the objective of the present work was to use lignin to agglutinate the tungsten powder particles to obtain an organic-metallic composite and to measure its linear attenuation coefficient of gamma radiation.

2. Materials and Methods

The following paragraphs describe the processing route to obtain of the composite of the W2.5%Lig and W5%Lig (in mass% of lignin). The procedure for obtaining the composites consisted of preparing homogeneous mixtures of the precursors, tungsten and kraft lignin in the proportions of 9.75:0.25 and 9.5:0.5, respectively.

*e-mail: armandocirilo@yahoo.com

The lignin was obtained from the black liquor of the kraft extraction process of cellulosic pulp[2]. The kraft black liquor lignin was removed and isolated via carbonation, then acidified at pH 2, see Figure 1. First, carbonic gas was bubbled into the hot black liquor; between 75% and 80% of the lignin was recovered by filtration. In the second step, the filtrate was treated with sulfuric acid; approximately 10% of the kraft lignin recovered as a powder[6].

Metal samples of powdered tungsten were used as precursors. The W powders were sieved and separated into several levels of granulometry using different sieves (200 μm and 250 μm) aiming to form a composite with a high degree of homogeneity[7-9]. For sample preparation, the precursors were weighed according to the desired mass ratios for the composition of the composites in mass proportions from 2.5% lignin to 97.5% tungsten and 5% lignin to 95% tungsten. Subsequently, the mixtures were homogenized and compacted in a 15-ton press at 450 MPa, which shaped samples 1.2 cm in diameter and 0.8 cm in height, as shown in Figure 2 after compaction.

The as compacted samples were sintered a quartz tube under mechanical vacuum, $1.5x10^{-1}$ Torr, under heating at a rate of 10 ºC.min^{-1} at two different temperatures 90 ºC and 100 ºC for elapsed times of 30 minutes. For comparison purpose, one sample was not sintered and it is identified in the present work as standard non sintered tungsten, or simply standard tungsten.

After the sintering, a 3D optical surface profiler was used to measure the samples surface roughness with nanometric scale. The Mx software was used for analysis.

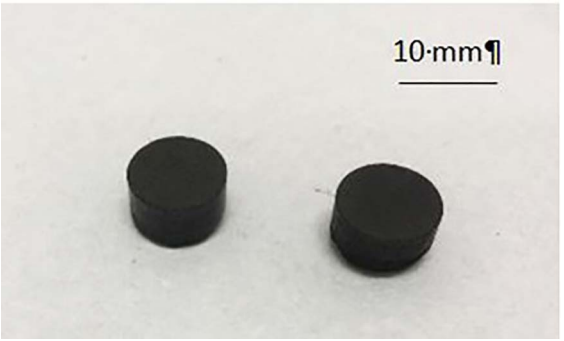

Figure 2. Optical image showing the samples of W2.5%Lig and W5%Lig after compaction at 440 MPa.

This software allowed complete system control and data analysis, including interactive 3D maps, quantitative topographic information, intuitive measurement navigation and embedded statistics routines, control charts and limits. This software was also used to determine the specific mass and porosity of the samples[11].

The experimental apparatus for measuring the gamma radiation attenuation was set up in the laboratory of Physics/USP and consisted of the following items: cobalt-emitting source, with two characteristic peaks at 1173 keV and 1332 keV; source containing seven cobalt pellets (Co-60) inside a lead vessel; a oscilloscope; a spectroscopic amplifier with a high voltage stabilizer source; XCOM software used to perform mathematical simulation of radiation phenomena; gamma emission detector as shown in Figure 3 a) and b).

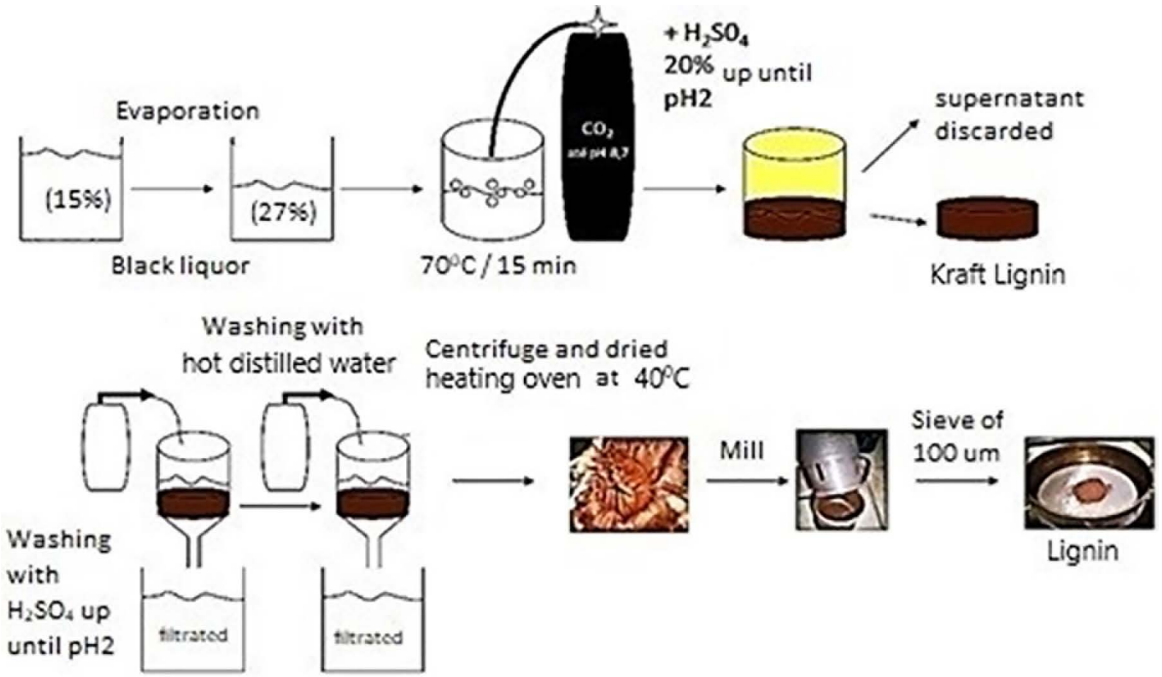

Figure 1. Experimental scheme of the kraft lignin obtention route. Adapted[8]

The methodology used to determine the linear attenuation coefficient was according to the Lambert-Beer law which is described by the equation: $I_x = I_o e^{-\mu x}$, where I_x is transmitted gamma rays beam intensity, I_0 is the initial gamma rays beam intensity, μ is the attenuation coefficient and x is the sample thickness.

3. Results and Discussion

The results from the 3D optical surface profilometer are shown in Figure 4, where the roughness and porosity of the W5%Lig samples after sintering at 90 ºC and 100 ºC in a limited area of 250 μm are depicted. The sample treated at 90 ºC had more pores, as inferred from the roughness values in terms of mean of the peak-to-valley roughness (Spv), than the sample treated at 100 ºC, Spv 39.7 μm and Spv 24.8 μm, respectively. This difference can be attributed to the increased temperature, melting and contraction of the lignin. It behaved as an adhesive between the metallic tungsten powder particles, decreasing the composite roughness.

Figure 5 compares the attenuation of gamma radiation spectra between an open source of Co-60 and the samples of standard tungsten and the composite W5%Lig sintered at 90 ºC. The results showed that at the two energy peaks characteristic of Co-60, a gradient in the attenuation coefficient around 32% between the open source radiation with no obstacles and standard tungsten; and around 42% between the open source radiation with no obstacle and the W5%Lig composite sintered at 90 ºC. Thus, the attenuation coefficient of the W5%Lig compound was higher than that of standard tungsten. This result may be attributable to the densification of the composite due to the concentration of lignin and the attenuation related to it. The presence of lignin decreases the sample porosity as temperature increases, i.e., there is a densification of the composite meaning that the distribution of the lignin surrounding the tungsten powder particles surface improves, thus increasing the absorption cross section and justifying the higher attenuation coefficient.

The Figure 6a represents the comparative spectra of the attenuation of gamma radiation among the samples of standard tungsten and the W5%Lig composite at different sintering temperatures. This outcome may be attributable to the degradation of the lignin as the temperature increases from 70 ºC to 90 ºC which showed the best gamma attenuation result, regarding the materials and conditions of the present work, and decreases for the sintering at 100 ºC, meaning that there is a degradation of the lignin composite matrix.

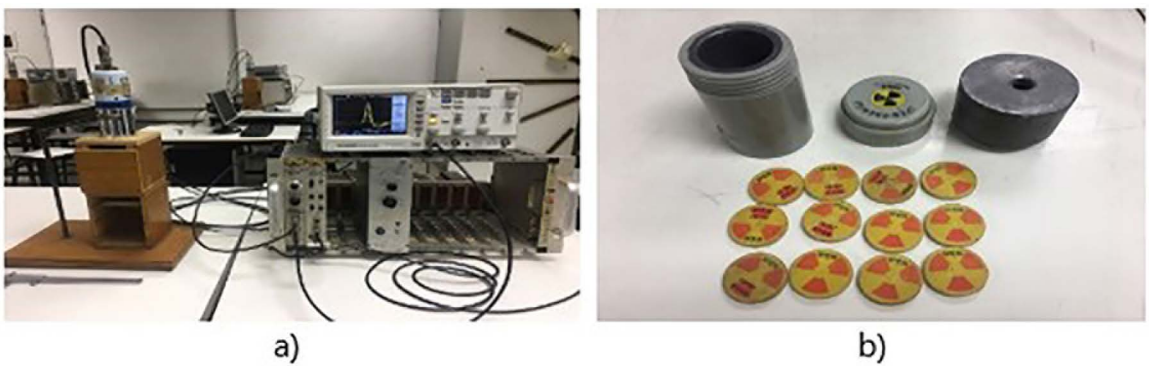

Figure 3. a) Experimental set up for gamma radiation attenuation. b) Cobalt source (Co-60).

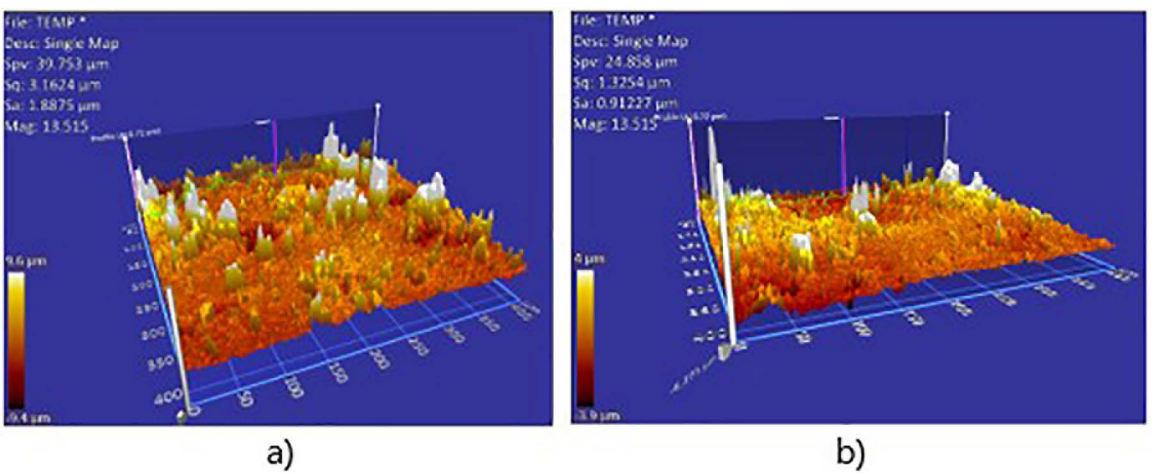

Figure 4. The optical profiles of the W5%Lig sample after sintering a) at 90 ºC and b) 100 ºC.

On the other direction, it was observed that the lignin shows good resistance to radiation degradation in its natural form[12-13]. Figure 6b represents the comparative spectrums of the attenuation of gamma radiation among the samples of standard tungsten and the W2.5%Lig and W5%Lig composites. The results show that changing the lignin concentration in the composite from 2.5% to 5% after the sintering process at 90 ºC did not cause a significant difference in the attenuation coefficient between then, see Figure 6b. This outcome shows that an even larger amount of lignin is needed so that a more significant difference in the attenuation coefficient can be achieved.

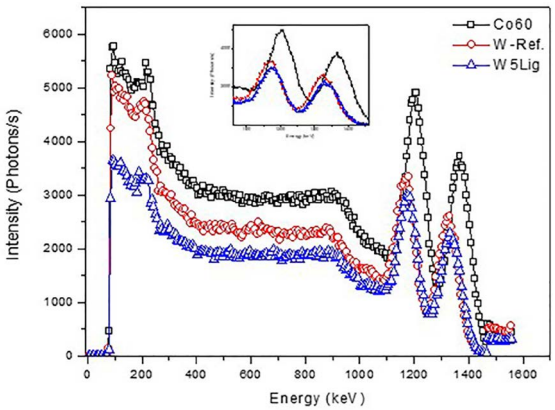

Figure 5. The comparative spectra of the attenuation of gamma radiation among Co-60, standard tungsten and W5%Lig sintered at 90 ºC.

In Table 1, it is showed that the coefficient of attenuation increases as the composite W5%Lig is sintered at 90 ºC, the coefficient of attenuation μ increases from 0.635 cm^{-1} for the reference tungsten to 0.832 cm^{-1} for the composite W5%Lig sintered at 90 ºC. This increase of 16% is attributed to the densification of the composite as function of the sintering temperature.

4. Conclusion

The present work to obtain of a metallic-organic composite using tungsten powder and lignin, showed promising results, the samples W2.5%Lig and W5%Lig presented good homogeneity and absence of degradation when sintered at temperatures up to 90 ºC, considering that lignin is an organic substance. The characterization by optical profilometry showed that the increase in temperature contributed to the agglutination of the tungsten particles, minimizing the porosity of the samples.

The evaluation of the interaction of gamma radiation with the samples to determine the attenuation coefficient between unobstructed open source of radiation and standard tungsten showed a gradient of 43% for the W5%Lig 90 ºC at the two Co-60 characteristic peaks.

The determination of the attenuation coefficients between reference tungsten and W5% Lig 90 ºC are different apart, therefore lignin besides playing the role of agglutinating the W particles it contributes to the attenuation, the linear

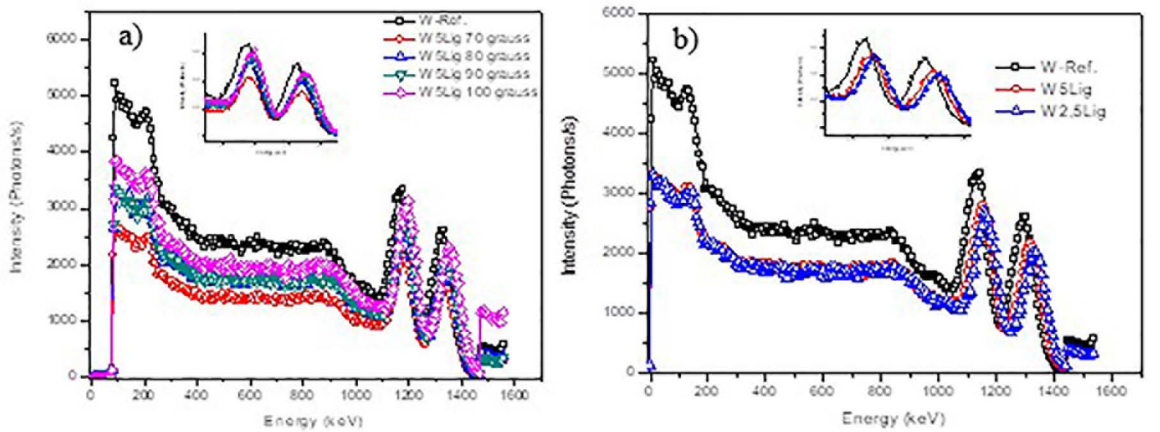

Figure 6. a) The comparative spectra of the attenuation of gamma radiation between standard tungsten and the W5%Lig composite sintered at different temperatures from 70 ºC to 100 ºC and b) The comparative spectra between standard tungsten and the W5%Lig and W2.5%Lig composites sintered at90 ºC.

Table 1. Coefficient of attenuation of gamma radiation for different samples of the composite W-lignin.

Sample	Incident photons (I_0)	Transmitted photons (I_x)	Ratio $\ln(I_0/I_x)$	Thickness x (cm)	Coefficient of attenuation μ (cm^{-1})
Co-60	4917	4917	0	-	-
W ref.	4917	3341	0.386	0.607	0.635
W5%Lig 90 ºC	4917	2795	0.564	0.679	0.832
W5%Lig 100 ºC	4917	3004	0.492	0.644	0.764

attenuation coefficient is 0.832 cm^{-1} for the W5%Lig 90 ºC sample with a thickness of 0.679 mm, so the results showed that the kraft lignin represents a choice to obtain of tungsten composite aiming its use as radiation shielding.

Measures of the attenuation coefficient of gamma radiation showed promising results; thus, this new composite may be useful as radiation shielding in the transportation of small quantities of highly radioactive substances, a need of the Institute of Energy and Nuclear Research of Brazil.

5. References

1. Suhas, Carrott PJM, Ribeiro Carrott MML. Lignin - from natural adsorbent to activated carbon: A review. *Bioresource Technology*. 2007;98(12):2301-2312.

2. Lawoko M, Henriksson G, Gellerstedt G. Structural Differences Between the Lignin-Carbohydrate Complexes Present in Wood and in Chemical Pulps. *Biomacromolecules*. 2005;6(6):3467-3473.

3. Wei X, Tang J, Ye N, Zhuo H. Novel preparation method for W-Cu composite powders. *Journal of Alloys and Compounds*. 2016;661:471-475.

4. Zakaryan M, Kirakosyan H, Aydinyan S, Kharatyan S. Combustion synthesis of W-Cu composite powders from oxide precursors with various proportions of metals. *International Journal of Refractory Metals and Hard Materials*. 2017;64:176-183.

5. Zhang L, Gellerstedt G. Quantitative 2D HSQC NMR determination of polymer structures by selecting suitable internal standard references. *Magnetic Resonance in Chemistry*. 2007;45(1):37-45.

6. Kim JY, Lee JH, Park J, Kim JK, An D, Song IK, et al. Catalytic pyrolysis of lignin over HZSM-5 catalysts: Effect of various parameters on the production of aromatic hydrocarbon. *Journal of Analytical and Applied Pyrolysis*. 2015;114:273-280.

7. Zivelonghi A, You JH. Mechanism of plastic damage and fracture of a particulate tungsten-reinforced copper composite: A microstructure-based finite element study. *Computational Materials Science*. 2014;84:318-326.

8. Gouvêa AFG. Production of the furniture industry waste and black liquor lignin from industry for the production of briquettes. [Doctorate Thesis]. Viçosa: Federal University of Viçosa; 2012. 101 p. (In Portuguese)

9. Gadelmawla ES, Koura MM, Maksoud TMA, Elewa IM, Soliman HH. Roughness parameters. *Journal of Materials Processing Technology*. 2002;123(1):133-145.

10. Ponomarev AV, Ershov BG. Radiation-induced high-temperature conversion of cellulose. *Molecules*. 2014;19(10):16877-16908.

11. Severiano LC, Lahr FAR, Bardi MAG, Santos AC, Machado LDB. Influence of gamma radiation on properties of common Brazilian wood species used in artwork. *Progress in Nuclear Energy*. 2010;52(8):730-734.

12. Ponomarev AV, Ershov BG. Fundamental aspects of radiation-thermal transformations of cellulose and plant biomass. *Russian Chemical Review*. 2012;81(10):918-935.

13. Sun J, Xu L, Ge M, Zhai M. Radiation degradation microcrystalline cellulose in solid status. *Journal of Applied Polymer Science*. 2013;127(3):1630-1636.