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# REOLOGICAL BEHAVIOR OF LIGNIN-HYBRID COMPOSITES LOTIONS WITH PHOTOPROTECTIVE PROPERTIES

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## ABSTRACT

The use of agro-industrial waste, such as cashew apple bagasse, appears as an economic and alternative source of lignin to use as a potential and natural UV blocker. Therefore, the present work aims to evaluate the reological behavior and photoprotective effects of lignin-hybrid composites with zinc and titanium oxides in sunscreen formulation. Lignin from cashew apple bagasse was first quaternized and combined with zinc acetate dihydrate or tetrabutyl titanate to composites production followed by its incorporation in emulsion base lotion. Results showed that although there was no increase in the SPF value of the emulsions with lignin composites compared to the emulsion with only lignin, a positive interaction of lignin-hybrid composites with the sunscreen components was demonstrated by rheology with UVA properties improvement. Furthermore, lignin-hybrid composites have shown to be a promising UV absorber even though other processes for composites production must be investigated.

**Keywords:** Lignin. Quaternization. Sunscreen. Titanium and Zinc Oxides. Photoprotective Properties.

## 1 INTRODUCTION

Due to the recent desire of the consumers in products with natural compounds, the search for natural compounds that can absorb UV (ultraviolet) radiation is of great interest. The dermocosmetics market is increasingly bringing sustainable products that take care of the consumer and do not harm the environment. Therefore, the importance of searching for low-cost photoprotective components from natural sources is noteworthy, which makes the use of agro-industrial residues, such as cashew apple bagasse, an economical and alternative source for lignin, a natural substance with photoprotective potential, non-toxic, biodegradable, cheap, and rich in aromatic rings that has protective properties in human tissue against ultraviolet radiation damage [1].

Excessive exposure to ultraviolet radiation is often discussed. The use of an appropriate UV photoprotector is generally desire to prevent the effects and risks of skin problems such as skin cancer, photoaging, burns and many diseases related to UV rays [2]. Organic and inorganic UV photoprotectors are abundantly used as active components to protect human skin from UV radiation within the dermocosmetics industries. Thus, with the cosmetic market searching for new natural UV absorbers, lignin, as a low-cost waste product and abundantly discarded by the cellulose and biorefinery industries, owning UV properties that are widely search by the dermocosmetics market. In this sense, it becomes an ideal candidate for use as an active ingredient in a sunscreen against UV radiation. Futhermore, its combination with active inorganic components such as $TiO_2$ and ZnO, will help provide better coverage against the sun UV spectrum range and also reduces the dark brown color of lignin to increase its applicability [3, 4, 5].

In the search for a sustainable product that protects skin, environmental friendly, low-cost and renewable, the present work aims to evaluate the compatibly of quaternized lignin-hibrid composites with $TiO_2$ and ZnO in sunscreen formulations by rheological behavior, and their photoprotective effects.

## 2 MATERIAL & METHODS

Lignin from cashew apple bagasse was firstly obtained according Rocha *et al.* (2009)[6] as black liquor and lignin precipitation was conducted as described by Serpa et al. (2020)[7]. The quaternized lignin-hybrid composites with ZnO (QALZnO) or $TiO_2$ ($QALTiO_2$) oxides was performed by Wang (2018, 2020)[8, 9]. A commercial lotion base without sun protection factor (SPF) was used to incorporate lignin and lignin-based composites. Sunscreens containing 10% (w/w) of active ingredients (Lignin, QALZnO, or $QALTiO_2$) were homogeneously dispersed using an Ultra-Turrax Tube Drive (IKA, Staufen, Germany) at 4,000 rpm for 10 min. The assessment of SPF was carried out in vitro using the spectrophotometric method, following the methodology described by Mansur *et al.* (1986)[10] with evaluation of the UVA/UVB ratio, with a scan of the absorbances of the solutions at wavelengths between 280nm and 400nm. Zeta Potential measurements were determined using Malvern 3000 Zetasizer NanoZS, (Malverne Instruments, UK) with susncreens samples dispersed in deionized water at 1:200 (m/m). All the rheological measurements were performed on a controlled-stress rheometer (HAAKE MARS, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a cone-and-plate geometry (C35/2° TiL) at constant temperature of 25 °C. An oscillatory rheology experiment was performed at 1 Hz during 4,00 minutes to estimate the dynamic viscosity ($\eta$), storage module ($G'$), and loss module ($G''$) of sunscreens. The thixotropy measurements were performed in a rotational experiment utilizing the previously described geometry. The shear rate was increased linearly from 0.001 to 450 $s^{-1}$ and the areas of thixotropy (defined as work performed for the demolition and

reconstruction of a sample inner structure) were computed by adding the areas between the “up” and “down” curves of the formulations studied.

## 3 RESULTS & DISCUSSION

The SPF of sunscreen formulations with lignin-hybrid composites were 1.7 for both lotions with QALZnO or QALTiO2. The sunscreen with only lignin (4.2) showed superior result. These data can be explained due to the broad UVB coverage attributed to lignin, which in composites appears in smaller proportions due to the presence of ZnO and TiO2 oxides, which have greater photoprotection properties in the UVA region. The UVA/UVB ration for lignin-hybrid composites was 1.9 and 2.1 for QALTiO2 and QALZnO sunscreens respectively, being superior to the sunscreen with only lignin (1.3). In this sense, the combination of lignin with oxides expands the photoprotection spectrum to the UVA region, which was not evidenced by Mansur et al. (1986)[10] equation.

The determination of Zeta Potential is one of the most common and important methods used to evaluate the stability of products. The formulations with QALZnO show better results (- 46.70 ± 1.17 mV) compared to susncreen with lignin (- 30.8 ± 1.85 mV) an the emulsion lotion only (- 38.8 ± 0.49 mV). The formulation with QALTiO$_2$ present + 0.28 ± 0.18 mV, indicating that QALTiO$_2$ composite are positively charged, probably due to a greater presence of $NH_4^+$ and $Ti^{4+}$ ions in the external region of the composite.

Figure 1 shows the results of the elastic (*G'*) and viscous (*G"*) modulus profiles of susncreens containing lotion base, lignin and quaternized lignin-hybrid composites. It is observed for all formulations, including the control, that the values of *G'* are higher than those of *G"* modulus, indicating that the lotions have a predominantly elastic profile[11]. This elastic behavior in the products shows that there was no change in the original characteristics of the control (emulsion base only).

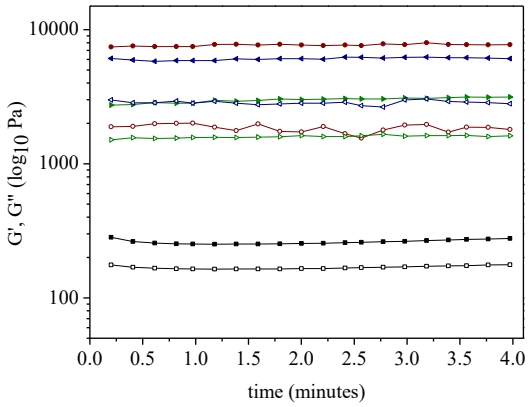


**Figure 1** Profile of the elastic modulus (*G'*) and viscous modulus (*G"*) of rheology with tension control obtained for formulations with lignin and quaternized lignin-hybrid composites with ZnO and TiO$_2$ at 10% (m/m). *G'* for control (■), lignin (●), QALZnO (◀) e QALTiO$_2$ (▶). *G"* for control (□), lignin (○), QALZnO (◁) and QALTiO$_2$ (▷).

Figure 2 presents the viscosity profiles with shear rate increasing of formulations. The lotions presented curves with a similar profile which indicate a typical behavior of a non-Newtonian fluid [12], characterized by a reduction in viscosity with an increase in shear rate. Besides this, it can be observed no relevant changes in viscosity behavior due to the addition of quaternized lignin-hybrid composites compared to control. However, in the case of the lotion containing only lignin, a noisy viscosity profile can be associated with sunscreen instability, confirmed at the end of the analysis, a separation of phases of the emulsion.

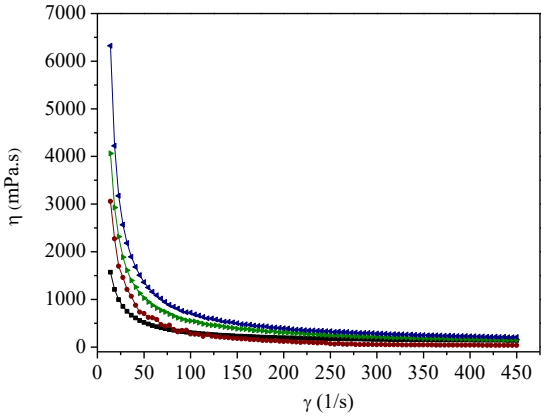


**Figure 2** Dynamic viscosity profile of formulations with lignin and quaternized lignin composites with ZnO and TiO$_2$ at 10% (m/m). Base emulsion (■), Lignin (●), QALZnO (◀) and QALTiO$_2$ (▶).

The rheological viscosity profile is closely associated to consistency and spreadability properties, one of the most important parameters when cosmetics are applied to human skin in real conditions of use [13]. Consistency can be assessed at low shear rates, while spreadability can be assessed subjectively at high shear rates [14]. In this sense, it can be seen that the addition of the composites (QALZnO and QALTiO$_2$) improved the consistency and did not affect the spreadability of the formulations, while the lignin protector changed the spreadability compared to the control. In this sense, the thixotropic profile was conducted only for formulations containing lignin composites (Figure 3).

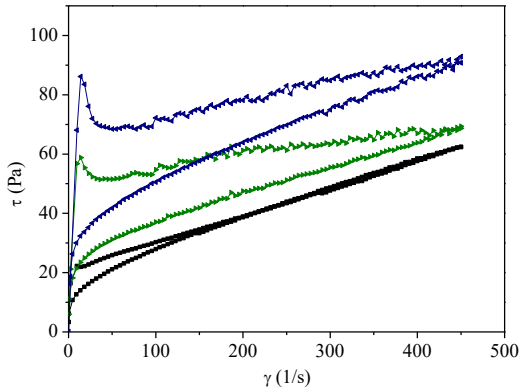


**Figure 3** Thixotropy of formulations with quaternized lignin-hybrid composites with $TiO_2$ and ZnO at 10% (m/m). Control (■), QALTi$O_2$ (►) and QALZnO (◄).

The rheograms (Figure 3) of QALZnO and QALTi$O_2$ show an increase in the thixotropy (area of hysteresis) of the formulations compared to the control. The control formulation showed thixotropy of 0.4 kPa/s while the sunscreens with lignin showed 6.4 and 5.5 kPa/s for QALZnO and QALTiO2, respectively. Products with thixotropy are easy to spread and be absorbed by the skin, which is important in cosmetics containing active substances [15]. Furthermore, it is noted that the value of the yield point from flow curves is higher in formulations with hybrid composites than in the control, suggesting a positive interaction with the sunscreen components, thus highlighting the importance of lignin conjugation in the form of lignin-hybrid composites.

## 4 CONCLUSION

Although quaternized lignin-based composites did not improve the SPF results of sunscreen formulations, these composites promoted a satisfactory stability of the cosmetic emulsion compared to the addition of only lignin based on rheological measurements. Furthermore, lignin-hybrid composites promoted better photoprotection in the UVA region, the range of UV radiation most susceptible to inducing skin diseases. In this sense, other studies should be conducted to improve the SPF coverage of lignin-based composites as well as the compatibility of these composites with other commercial UV absorbers.

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