

# *Rheological behavior of magnetic pulp fiber suspensions*

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**ABSTRACT:** This paper is focused on the rheology of magnetic pulp suspensions in absence and presence of an external magnetic field. Magnetic fibers were prepared by the lumen loading method using bleached eucalyptus fibers and cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles. The effect of mass consistency, temperature, concentration of magnetic fibers, and magnetic field strength on yield stress and apparent viscosity of the suspensions were investigated. In the absence of an applied field, a dependence of yield stress with consistency, as well as with the percentage of magnetic fibers present in the suspension, was found. In flow tests, all the suspensions exhibited shear-thinning behavior, showing that the viscosity is only affected by the consistency of the suspension. On the other hand, magnetorheological measurements show a negative effect of the applied magnetic field on the viscosity of the suspension.

**Application:** The modification of cellulose fibers with magnetic particles offers a series of advantages that range from the possibility of manipulating the orientation and flocculation of suspended fibers to its use in the production of magnetic paper for the purposes of coding and storage, multi-printing, and magnetic protection, among

Pulp suspensions consist of wood or other lignocellulosic fibers broken down by physical or chemical processes, dispersed in water [1]. This type of suspension exhibits complex rheological behavior due to the presence of flexible and thin fibers, which can form networks that tend to flocculate and help to transmit stresses, resulting in non-Newtonian behavior. Therefore, fiber suspensions may show a variety of rheological phenomena, e.g., yield stress, shear thinning, shear thickening, thixotropy, extensional effects, viscoelasticity, etc. [2,3]. This behavior has practical implications in many stages of the papermaking process; for instance, during the transport of fiber suspensions and the forming of paper [4]. The incorporation of magnetic nanoparticles to fibers gives them the ability to respond to external magnetic fields [5], so many of their flow properties as well as those of the finished product, can be controlled or manipulated.

Within the rheological properties, yield stress and viscosity are the most important for the design of process equipment in the paper industry. In the case of unmodified lignocellulosic fibers, some results about rheological behavior of pulp suspensions have been reported in the literature. Thus, Bennington, Kerekes, and Grace [6] determined the yield stress for commercial wood pulp suspensions of low and medium consistency. The yield stress was found to be accurately correlated with the volumetric concentration of the suspension using equations of the form. Later, Dalpke and Kerekes [7] determined that the yield stress of pulps of different species increased with consistency and fiber length. Additionally, a decreasing of yield stress with temperature in the interval of  $25^\circ\text{C}$ – $40^\circ\text{C}$  was determined by Sánchez, Quintana and Fajardo [8] for bleached sugarcane

bagasse suspensions. On the other hand, cellulose fiber suspensions exhibit shear-thinning behavior, as have been observed for pulp suspensions from eucalyptus [9], pine [10], and sugarcane bagasse [8]. It was found further that apparent viscosity increases with consistency but decreases with temperature. Chen, Tatsumi, and Matsumoto [11,12] performed measurements of shear stress of hardwood bleached kraft pulp over a range of shear rates from 0.1 to  $100\text{ s}^{-1}$ . They observed Newtonian behavior at low shear rates, unstable behavior at medium shear rates due to formation of flocs, and Newtonian behavior once shear rates were high enough to disperse the flocs. Furthermore, they also noticed that longer fibers increased the flocculation tendency, as compared to shorter fibers. Derakhshandeh, Hatzikiriakos, and Bennington [13] found that pulp suspensions exhibited shear-thinning behavior up to a critical shear rate value, after which the suspension exhibited Newtonian behavior. Suspension viscosity increased with increasing consistency, fiber length, and pH. In the Newtonian regime at high shear rates, the viscosity was found to vary with the consistency to the third power. Finally, reviews on the rheology and flow properties of pulp suspensions have been reported by Kerekes [3], Cui [14], and Derakhshandeh [2].

Most research studies on the subject of magnetic cellulose fibers have focused on their preparation and characterization. However, to the best of our knowledge, experiments showing the rheological behavior of these suspensions, in absence or presence of a magnetic field, have not been reported. Magnetic fibers can be obtained via loading method, which consists of introducing magnetic nanoparticles inside the lumen of the fibers by a physical deposition process [15]. Since the magnetic properties

of fibers are improved as the loading degree of particles increases [16-18], they are able to be manipulated by the application of an external magnetic field. Hence, Marchessault et al. [19] found that suspended magnetic cellulose fibers obtained by the lumen loading method tend to align in a magnetic field and that the anisotropy of the fibers can be hydrodynamically controlled to obtain axially oriented paper. Likewise, Mashkour et al. [20] obtained unidirectional magnetic paper using permanent magnets with low intensities. Their results indicate that, at lower concentrations, a better alignment of the fibers is achieved due to greater space for the free rotation of the fibers; in addition, the obtained paper shows anisotropic magnetic and mechanical properties. On the other hand, the magnetorheology of magnetic fiber suspensions was studied theoretically and experimentally by Lopez-Lopez et al. [21] and Kuzhir et al. [22] for cobalt microfiber suspensions. Their findings show a controllable yield stress with the applied magnetic field, which can be 2 to 3 times higher than that of a cobalt microspheres suspension. Additionally, they observed that, under the action of a magnetic field, the fiber network tends to align, but the friction between the fibers does not allow a complete alignment along the field direction. The latter was also evidenced by Morillas et al. [23] for rigid magnetic particles of large aspect ratios.

In this paper, we present experimental results concerning the rheology and magnetorheology of magnetic cellulose fiber suspensions. Magnetic fibers were prepared by the lumen loading method using bleached eucalyptus pulp and cobalt ferrite nanoparticles ( $\text{CoFe}_2\text{O}_4$ ). The effect of mass concentration, temperature and magnetic field on yield stress and apparent viscosity of the suspension was studied using a stress-controlled rheometer. Mathematical models were proposed to correlate apparent viscosity with shear rate.

## MATERIALS AND METHODS

### Materials

All chemical reagents were used as received from suppliers. Iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 97 wt%) from Merck (Kenilworth, NJ, USA); cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 99 wt%) from Panreac Applichem (Chicago, IL, USA); sodium hydroxide (NaOH, 97 wt%) from Merck; and ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ , 97wt%) from Merck were used to synthesize the magnetic nanoparticles. Cellulose fibers were obtained from bleached eucalyptus pulp supplied by a local company, and polyethylenimine branched ( $(\text{H}(\text{NHCH}_2\text{CH}_2)_n\text{NH}_2)$ , 99 wt%) from Sigma-Aldrich (St. Louis, MO, USA), with a mass-average molecular weight of 10000 g/mol, was used as retention aid. All the solutions and suspensions were prepared with distilled water.

### Synthesis of cobalt ferrite nanoparticles

Cobalt ferrite nanoparticles were synthesized by the coprecipitation method [24], and 100 mL of an aqueous solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.4 M) was added to 100 mL of an aqueous

solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.2 M). This mixture was heated up to 60°C and stirred at 150 rpm. Then, 100 mL of NaOH solution (6 M) were added as precipitating agent, turning the solution into a black color, indicating the formation of cobalt ferrite. The total time of synthesis was 1 h. After cooling to room temperature, nanoparticles were decanted using a permanent magnet, washed twice with distilled water and ethanol, and dried at 60°C overnight.

### Modification of eucalyptus fibers with cobalt ferrite nanoparticles

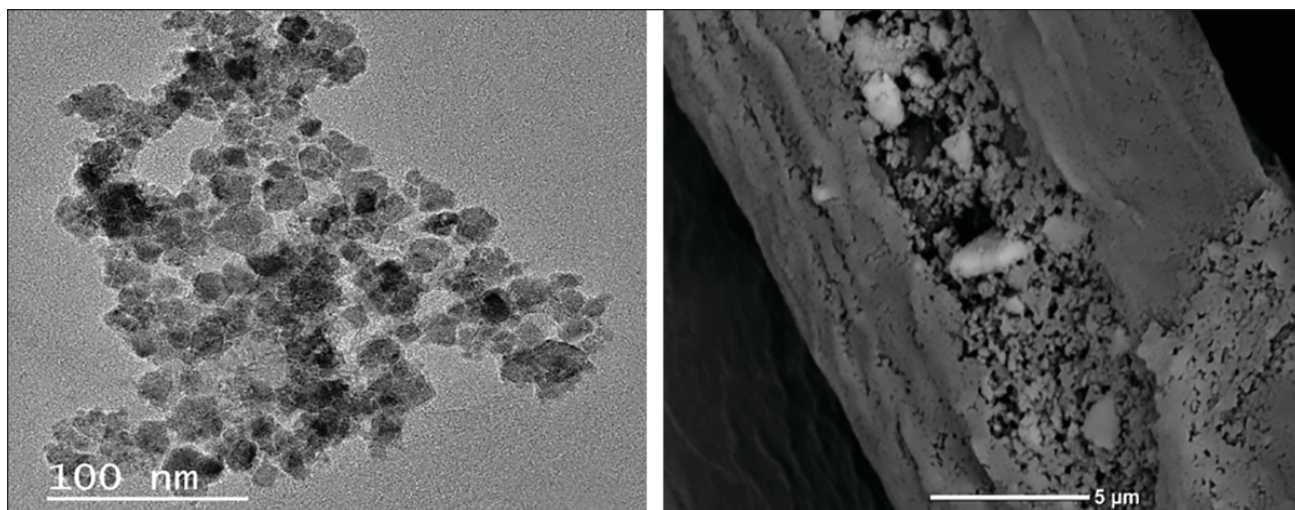
Magnetic fibers (MF) were obtained by lumen loading method [15]. First, eucalyptus pulp was disintegrated in distilled water using a JSR disintegrator (JSR Instruments; Roorkee, India) according to TAPPI Standard Test Method T 205 sp-02 "Forming handsheets for physical tests of pulp." Then, the fibers suspension 1.2 wt% was mixed with cobalt ferrite nanoparticles (mass ratio 1:1 based on dry pulp) and stirred constantly at 400 rpm for 60 min. Later, and in order to improve the retention of nanoparticles in the fibers' lumen, polyethylenimine (2% based on dry pulp) was added to the suspension under continuous stirring at 400 rpm for 4 h. The final suspension was carefully subjected to a flotation process in order to separate the modified fibers from the nanoparticles that were not incorporated into fibers. Finally, the magnetic fibers were washed in a sieve mesh with tap water for approximately 20 min and then dried at 60°C for 24 h.

### Physicochemical characterization

Cellulose fibers were morphologically characterized using a MORFI Compact ISO/FDIS 16065-2 analyzer (Techpap; Gières, France). Cobalt ferrite nanoparticles were morphologically and structurally characterized by transmission electron microscopy (TEM) using a Tecnai F-20 Super Twin 200 kv microscope (FEI Company; Hillsboro, OR, USA). To verify the incorporation of the nanoparticles into fibers, MF were analyzed by scanning electron microscopy (SEM) in a JCM-6000 Plus microscope (JEOL Ltd; Tokyo, Japan). The loading degree of nanoparticles was estimated by the ash content according to TAPPI T 211 "Ash in wood, pulp, paper and paperboard: combustion at 525°C." Magnetic properties of the magnetic particles, as well as those of the modified fibers, were measured by a vibrating sample magnetometer (Quantum Design; San Diego, CA, USA) at 300 K.

### Rheological experiments

Rheological measurements, without magnetic field applied, were performed in a DHR-2 rheometer (TA Instruments; New Castle, DE, USA) using a concentric cylinder cup (30-mm diameter) with a four-bladed vane rotor (15-mm diameter). The rotor diameter guarantees a gap between blades and housing larger than five times the characteristic size of the suspended particles [7]. A Peltier temperature control system was used to keep the temperature at 25°C and 50°C. Suspensions with 0% (NMF), 50% (MF50), and 100% (MF100) of magnetic fibers



**1. Transmission electron microscopy (TEM) of the cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles (left). Scanning electron microscopy (SEM) image for cellulose fibers loaded with  $\text{CoFe}_2\text{O}_4$  nanoparticles (right).**

were evaluated at consistencies of  $C_m = 1.0, 2.5$ , and  $4.0 \text{ wt\%}$ . In order to erase any previous shear history, all samples were pre-sheared with a shear rate of  $200 \text{ s}^{-1}$  for 60 s. Afterward, the sample was kept at rest to recover part of its structure. Static yield stress of fiber suspensions was determined by oscillatory strain-sweep [25] at a frequency of 1.0 Hz, recording the in-phase component of the oscillatory stress  $\tau' = G'\gamma$ . The yield stress value was obtained from the point of deviation from linearity of a log-log plot. For the apparent viscosity, a steady flow curve was obtained by performing a shear rate-sweep between 0.2 and  $400 \text{ s}^{-1}$ , where each experimental point was recorded after a steady state viscosity was reached, i.e.,  $d\eta/dt \leq 0.05 \text{ Pa}$ .

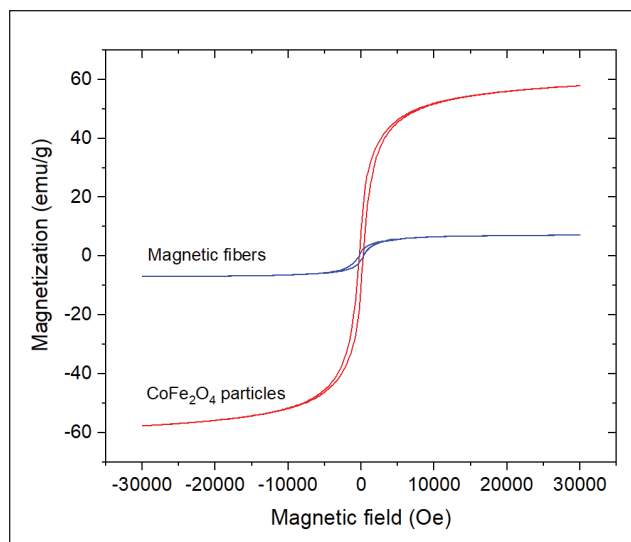
### Magnetorheological experiments

Magnetorheological measurements were performed in an MCR 302 rheometer (Anton Paar; Graz, Austria) at  $25^\circ\text{C}$  using a parallel plate geometry with a diameter of 20 mm and a magnetic field strength of  $H = 2100 \text{ G}$ . Given that aqueous suspensions of cellulose fibers tend to settle, magnetic fibers were then suspended in a 70% glycerol-in-water mixture in order to guarantee certain stability of the suspensions during tests. Furthermore, to prevent the suspension from being squeezed out of the geometry, and with the aim to keep the magnetic field as uniform as possible, the gap used was 2.0 mm. Static yield stress was determined by oscillatory strain-sweep, as mentioned above, and the steady flow curve was determined by a shear rate-sweep between 0.1 and  $100 \text{ s}^{-1}$ .

## RESULTS AND DISCUSSION

### Physicochemical characterization

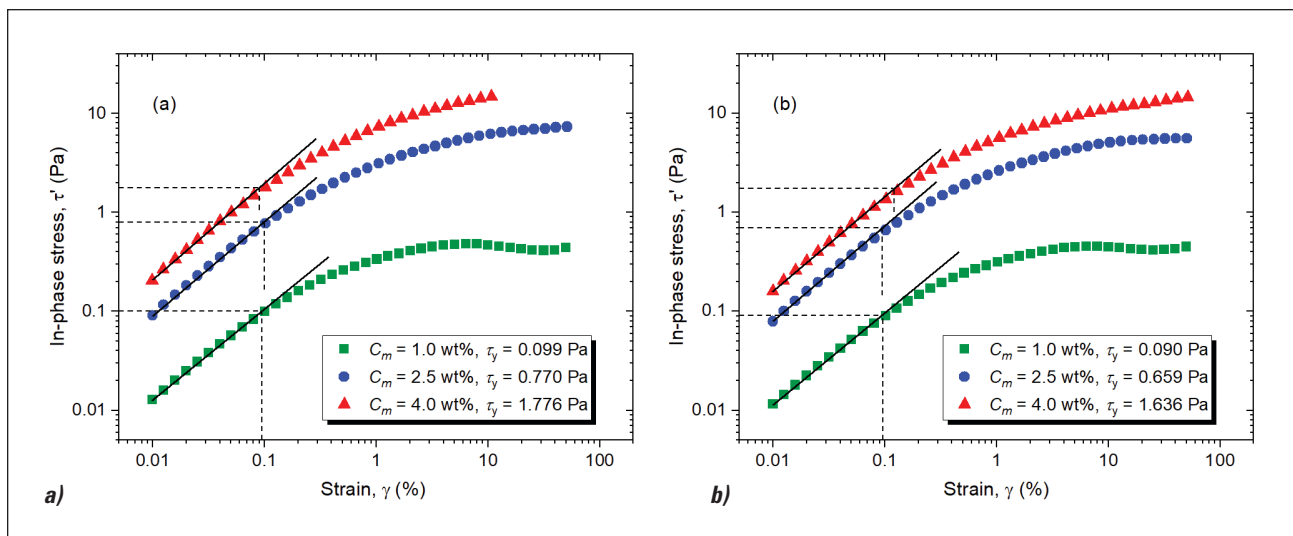
Morphological characterization of the eucalyptus pulp indicates that the cellulose fibers have an average length and diameter of 0.8 mm and  $17 \mu\text{m}$ , respectively, as well as a coarseness of  $0.0658 \text{ mg/m}$ . **Figure 1** shows a TEM for the



**2. Magnetization hysteresis loops at 300 K for  $\text{CoFe}_2\text{O}_4$  nanoparticles and magnetic fibers. The magnetization is referred to as the total weight of the sample.**

cobalt ferrite nanoparticles and an SEM image of a modified cellulose fiber. As can be seen, the nanoparticles have an irregular and polydisperse morphology, having an average diameter of 11 nm. Moreover, the nanoparticles appear to be incorporated in the lumen of the fibers, because it is unavoidable that some particles are deposited on the surface of these. According to the ash content of the modified fibers, a particle loading degree of approximately 14 wt% was found, which is similar with the results obtained by Wu et al. [17] and Chia et al. [16] for iron oxide black ( $\text{Fe}_3\text{O}_4$ ), who achieved 13 wt% and 22 wt% of magnetic material loading, respectively.

On the other hand, magnetic properties of nanoparticles and magnetic fibers are shown in **Fig. 2**. A narrow hysteresis loop is observed for both samples, indicating ferromagnetic behavior. The particles further show a saturation mag-



**3. Representative plots of the in-phase component of oscillatory stress vs. strain for suspensions with 50% of magnetic fibers (MF50) at different consistencies ( $C_m$ ) and temperatures: (a) 25°C, and (b) 50°C.**

netization of 57 emu/g, whereas the magnetic fibers reach a maximum value of 7 emu/g. This discrepancy in the saturation value is probably due to the fact that nanoparticles are “protected” by the fiber’s cell walls and they are immobilized into the lumen of the fiber. Therefore, the particles are hindered to align along the magnetic field direction, decreasing the intensity of the magnetic signal without losing their sensitivity to respond to magnetic fields [17, 19].

## Rheological experiments

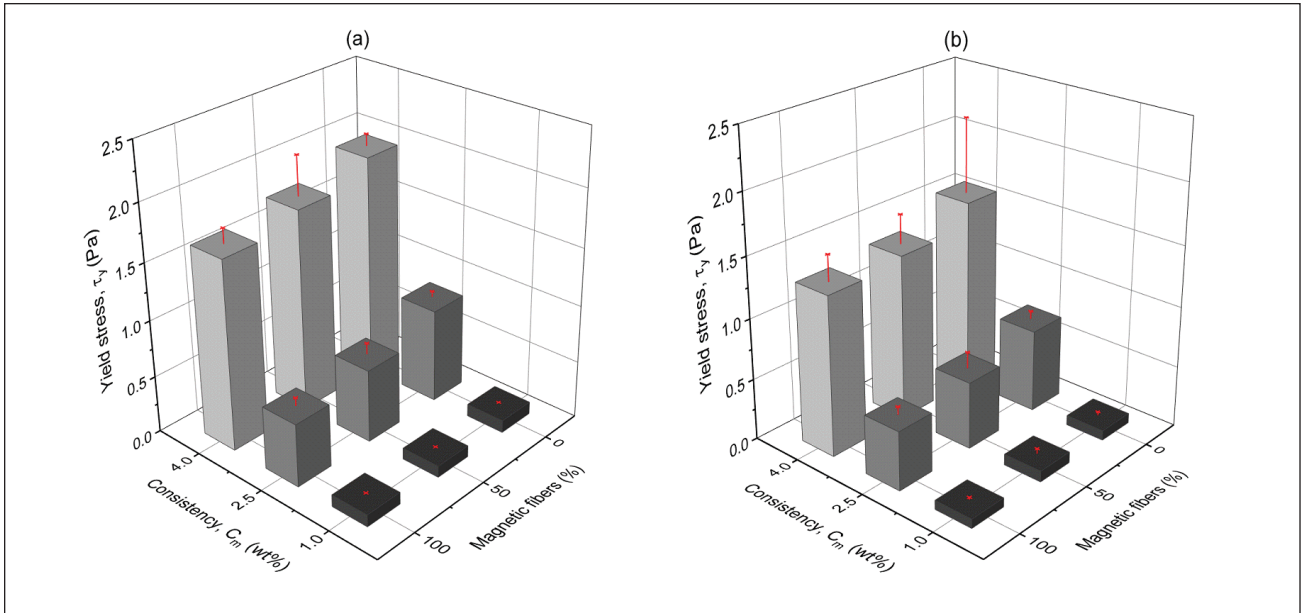
As the yield stress is simply the stress required to exceed a critical strain, an oscillatory strain-sweep provides a well-controlled way to obtain the yield point of the fiber suspensions. **Figure 3** shows representative results of the test performed. As the deformation increases, a proportional increase in oscillatory stress is observed up to a critical point, where it deviates from linearity, which is referred to as the apparent yield point or yield stress  $\tau_y$ . No significant change of the internal structure occurs below the yield point; therefore, the suspension shows a gel-like behavior. Once the deformation overcomes the critical point, the structure “breaks” and the material progressively begins to yield.

**Figure 4** shows the yield stress as a function of the mass consistency and the percentage of modified fibers in the suspension. As observed, there is an increase of yield stress with the consistency of the suspension, probably due to a higher flocculation of the suspension. The potential of the suspension to form flocs can be determined by the “crowding number,”  $N$ , which represents the number of fibers within a spherical volume of diameter equal to the length of a fiber, as shown in Eq. 1 [26]:

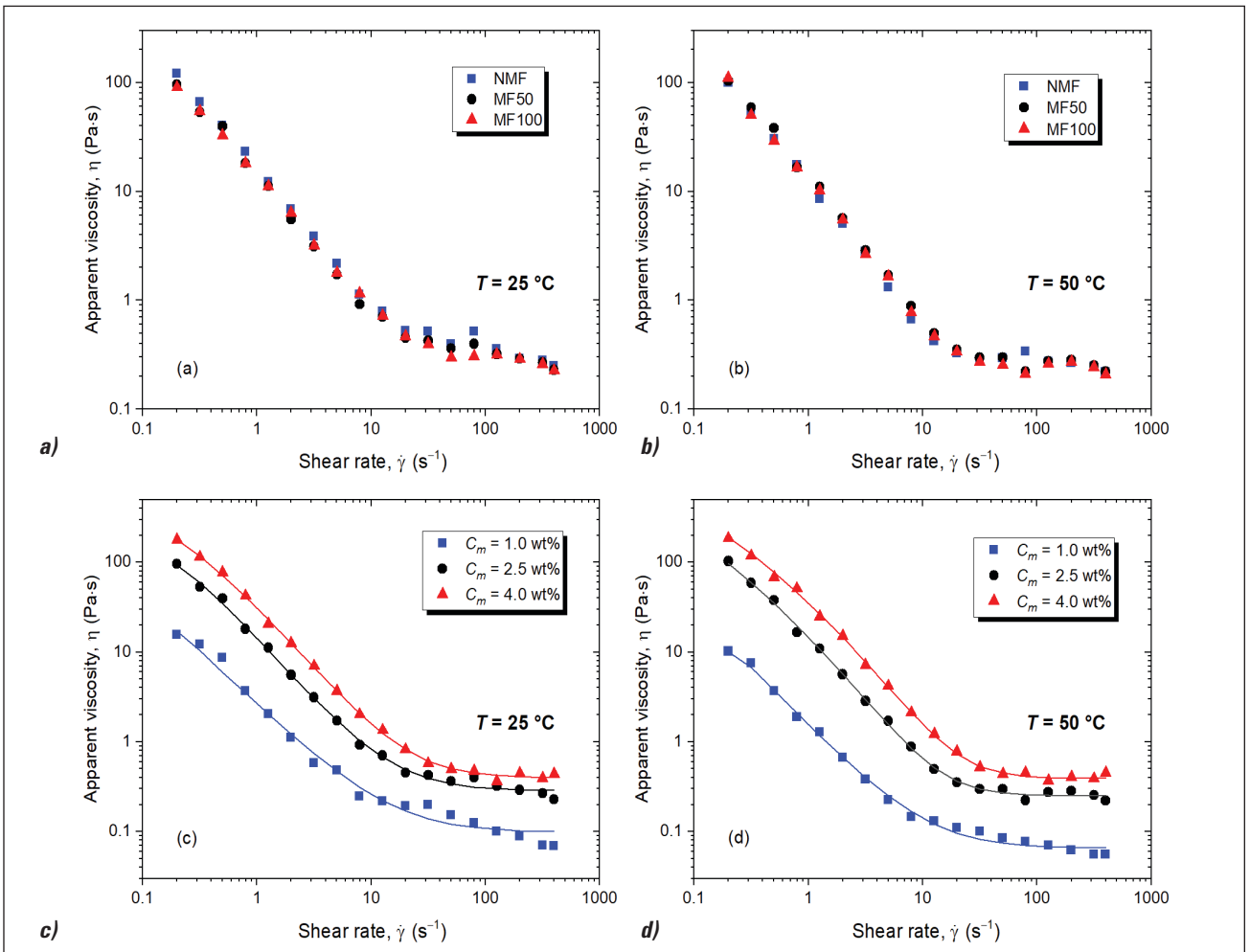
$$N = 5C_m \frac{L^2}{\omega} \quad (1)$$

where  $C_m$  is the suspension mass consistency (%),  $L$  is the fiber length (m), and  $\omega$  is the fiber coarseness (kg/m). In this work, and according to the consistencies evaluated ( $C_m = 1.0$  wt%, 2.5 wt%, and 4.0 wt%), the crowding number of the suspensions was of  $N = 39$ , 97, and 155, respectively. It has been reported that suspensions in the range  $16 < N < 60$  form a continuous network of fibers where the flocs behave as loose aggregates [27,28]. On the other hand, suspensions with  $N > 60$  develop significant mechanical strength and rigidity due to more inter-fiber contact within flocs and around them [26]. Hence, at higher consistencies, the number of contacts between fibers increases the friction and entanglements in the fiber network, which promotes formation of flocs and an increase in the resistance to start flow [2, 8, 29]. These results show the same trend as those obtained by Benington et al. [6] and Dalpke and Kerekes [7] about the effect of consistency on yield stress of suspensions of non-modified fibers. However, our yield stress values are considerably lower, perhaps due to the measuring technique employed.

The yield stress of the suspension was also affected by the incorporation of magnetic fibers, since it shows an inversely proportional relationship with the percentage of magnetic fibers present in the suspension. It has been observed that the addition of chemical additives can influence the flocculation of the fibers by altering the friction between them [30], which affects the rheology of the suspension [31]. Hence, the presence of magnetic fibers can affect the formation of flocs in the fiber suspension, which could be attributed to the presence of remaining nanoparticles on the external surface after the washing process [32]. This fact causes a disruption of inter-fiber cohesion, probably due to a steric hindrance and electrostatic repulsion between negatively charged particles [33]. Moreover, the incorporation of particles into fibers can cause some stiffness



**4. Apparent yield stress as a function of consistency and percentage of modified fibers present in the suspension at different temperatures: (a) 25°C, and (b) 50°C.**



**5. Steady apparent viscosity curves at 25°C and 50°C: (a, b) effect of the magnetic fibers' percentage,  $C_m = 2.5$  wt%; and (c,d) effect of consistency in suspensions with 50 wt% of magnetic fibers (MF50). Solid lines represent Carreau-Yasuda model.**

| Sample | $C_m$ ,<br>wt% | $\eta_{\infty}$<br>Pa·s |          | $\eta_0$ ,<br>Pa·s |      | $\lambda$ ,<br>s |        | $n$   |        | $a$   |       |
|--------|----------------|-------------------------|----------|--------------------|------|------------------|--------|-------|--------|-------|-------|
|        |                | 25°C                    | 50°C     | 25°C               | 50°C | 25°C             | 50°C   | 25°C  | 50°C   | 25°C  | 50°C  |
| NMF    | 1.0            | 40.47                   | 29.13    | 0.09               | 0.08 | 13.67            | 7.54   | -0.12 | -0.43  | 12.58 | 2.35  |
|        | 2.5            | 267.21                  | 109.26   | 0.33               | 0.27 | 6.57             | 4.47   | -0.43 | -0.44  | 1.57  | 58.20 |
|        | 4.0            | 1032.93                 | 24506.00 | 0.51               | 0.42 | 9.11             | 0.46   | -0.36 | -1.74  | 1.24  | 0.25  |
| MF50   | 1.0            | 17.53                   | 10.16    | 0.10               | 0.07 | 4.92             | 4.35   | -0.20 | -0.30  | 33.58 | 68.33 |
|        | 2.5            | 186.18                  | 12558.70 | 0.29               | 0.25 | 6.00             | 0.58   | -0.42 | -1.88  | 1.76  | 0.27  |
|        | 4.0            | 629.36                  | 5311.30  | 0.40               | 0.39 | 6.45             | 0.44   | -0.50 | -1.80  | 0.98  | 0.32  |
| MF100  | 1.0            | 28.92                   | 28.85    | 0.08               | 0.08 | 8.29             | 6.77   | -0.17 | -0.33  | 2.15  | 1.60  |
|        | 2.5            | 965.96                  | 59375.00 | 0.26               | 0.23 | 15.07            | 5.E-08 | -0.46 | -18.23 | 0.70  | 0.16  |
|        | 4.0            | 24636.60                | 33304.20 | 0.42               | 0.33 | 0.31             | 2.E-10 | -1.86 | -60.24 | 0.24  | 0.17  |

NMF = 0% magnetic fibers; MF50 = 50% magnetic fibers; MF100 = 100% magnetic fibers;  $C_m$  = suspension mass consistency;  $\eta_0$  = zero-shear viscosity;  $\eta_{\infty}$  = infinite-shear viscosity;  $\lambda$  = time constant;  $a$  = constant indicating transition to the decreasing portion of the viscosity; and  $n$  = power-law-like index.

## I. Parameters of the Carreau-Yasuda model for suspensions with non-magnetic and magnetic fibers.

in them [34, 35], reducing the number of contacts between fibers and thus the strength of the network structure [36]. On the other hand, although an increase in temperature could reduce the yield stress that is attributed to less energy required to break up the fiber networks and to overcome friction between flocs [37], the experimental results do not show a statistically significant difference in the range of temperature evaluated, i.e., 25°C to 50°C.

Apparent viscosity of pulp suspensions was recorded as a function of shear rate at different consistencies and temperatures. **Figure 5** shows the effect of magnetic fibers' concentration and consistency on the apparent viscosity of the suspension at 25°C and 50°C. A shear-thinning behavior (i.e., a decrease of apparent viscosity with increasing shear rate) is observed, where the viscosity is independent of the magnetic fibers' concentration but increases with the consistency of the suspension (analogous results were obtained for other consistencies and concentrations of magnetic fibers). This thinning behavior has been experimentally evidenced for suspensions of non-magnetic cellulose fibers from eucalyptus and pine bleached kraft pulps [9], bleached softwood fibers [38], and bleached sugarcane bagasse [8].

The flow curves show a high viscosity at the starting point, where the flocs start to form and cause a series of inter-fiber collisions and a stronger fiber network, which imparts resistance to flow [12]. By increasing the shear rate, the breakdown of fiber networks and fiber flocs by shear forces allows the suspension to flow easier, resulting in a decrease in viscosity [13]. This provokes the pulp suspension to thin over a wide range of shear rates. At certain high-shear rate values, the suspensions exhibit a tendency to a Newtonian behavior, which is called the turbulent or fluidization state [39,40]. At this point, the network struc-

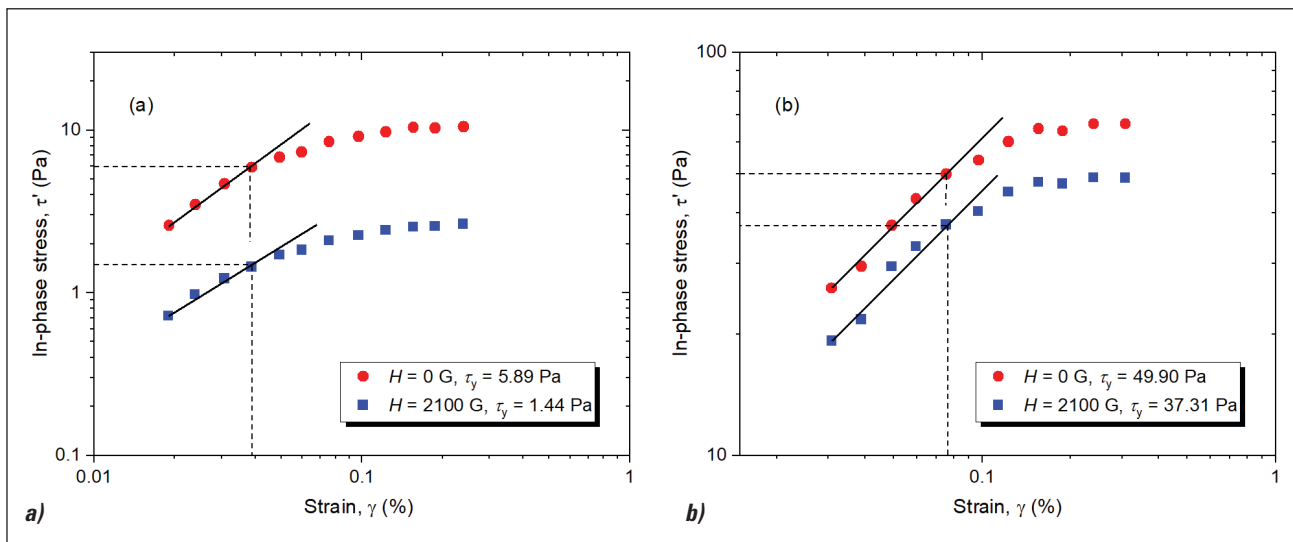
ture is disrupted and sheared strongly in all directions, while individual fibers and flocs move randomly in the suspension, causing a significant reduction in the viscosity [13]. The shear rate (shear stress) for the onset of fluidization is a critical operating parameter for the pulp and paper industry, as this is related to less energy consumption in pulp processing [40]. On the other hand, Fig. 5 also shows that the apparent viscosity of the suspensions increases with the consistency of the suspension. This fact is probably due the higher concentration of fibers, which implies a higher crowding number and favors more collisions through translation in shearing flow, creating mechanical strength in the network [28]. Similar results were found by Silveira et al. [9] for suspensions of non-modified eucalyptus fibers. They showed that the viscosity of the suspensions increases with both consistency and fiber length. Furthermore, their reported values are within the ranges determined by our experiments.

In order to obtain mathematical expressions for apparent viscosity, the Carreau-Yasuda model (Eq. 2) was fitted to the experimental data:

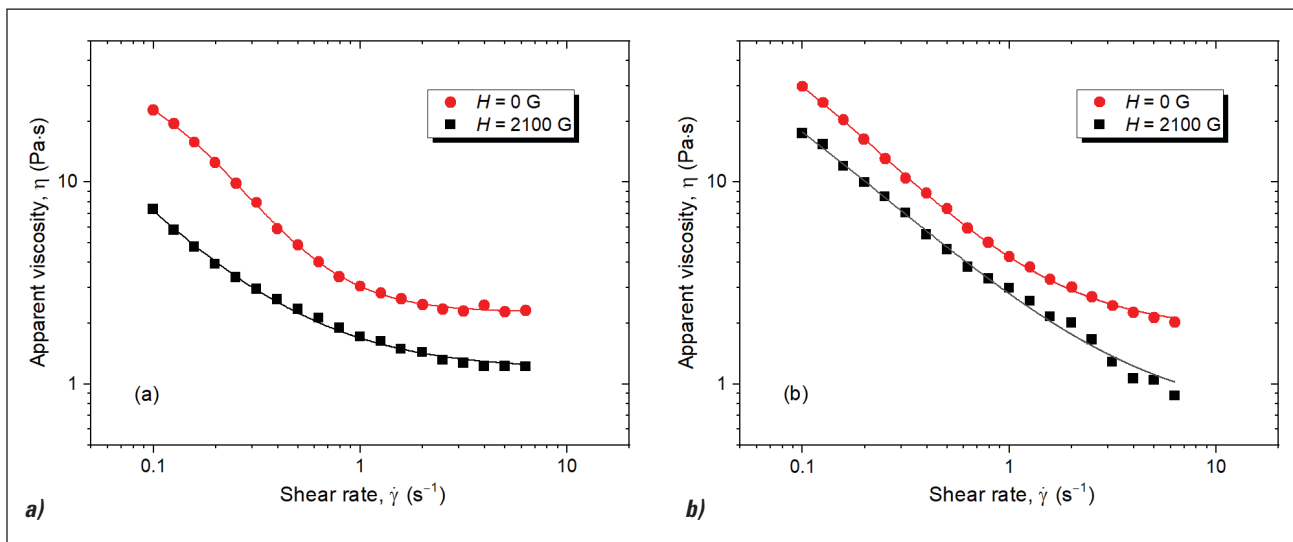
$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \left[ 1 + (\dot{\gamma}\lambda)^a \right]^{\frac{n-1}{a}} \quad (2)$$

where  $\eta_{\infty}$  is the infinite-shear viscosity,  $\eta_0$  is the zero-shear viscosity,  $\gamma$  is a time constant,  $a$  is a constant indicating the transition to the decreasing portion of the viscosity, and  $n$  is a power-law-like index. The fitting parameters of Eq. 1 are summarized in **Table I**.

As seen in Fig. 3, the Carreau-Yasuda model fits the experimental data well. However, some overly high values of zero-shear viscosity are observed, which is a consequence



**6. In-phase component of oscillatory stress vs. strain for suspensions of magnetic-fibers/glycerol in absence and presence of an external magnetic field: (a)  $C_m = 1.0$  wt%, and (b)  $C_m = 2.0$  wt%.**



**7. Steady apparent viscosity curves for suspensions of magnetic-fibers/glycerol in presence of an external magnetic field: (a)  $C_m = 1.0$  wt% and (b)  $C_m = 2.0$  wt%. Solid lines represent Cross model.**

of the fitting process in the data range analyzed, along with the inexistence of an experimental Newtonian plateau at low shear rates. Zero-shear viscosity is associated with the ability of the suspension to avoid sedimentation when stored. On the other hand, the apparent viscosity was not significantly affected by temperature (Fig. 3). This fact was also evidenced by Ferreira et al. [10] and Sánchez et al. [8], who reported viscosity values that do not show a statistically significant difference as a function of temperature.

Contrary to observations regarding yield stress, the concentration of magnetic fibers did not appreciably affect the apparent viscosity of the suspension, as seen in Figs. 3a and 3b. This indicates that the incorporation of magnetic fibers to the suspension does not alter its fluidity, which would allow the use of this material in productive processes with-

out modifying its flow behavior in relation to traditional pulp suspensions.

### Magnetorheological experiments

With the aim of analyzing the magnetorheological effect of magnetic fiber suspensions, the static yield stress was determined by plotting the in-phase component of oscillatory stress as a function of strain (**Fig. 6**), in the same way as for rheological experiments. In absence of a magnetic field, the yield stress values are higher than those predicted by the model obtained by Swering et al. [41] for non-magnetic pulp ( $\tau_y = 1.11C_m^{2.6}$ ) using a parallel plate viscometer. This discrepancy is attributed to the high viscosity of the glycerol-in-water mixture used as suspending medium. On the other hand, yield stress decreases when the external mag-

netic field is applied, with this effect being more noticeable at a lower consistency. Thus, a reduction of around 70% in yield stress was obtained for a 1.0 wt% suspension, whereas for a 2.0 wt% suspension, the reduction was 25%. This negative effect of the magnetic field on yield stress is probably due to the fact that part of each fiber becomes straight when the incorporated particles tend to align along the magnetic field, causing fibers to turn stiffer. Although it is unlikely that fibers straighten completely, this induced rigidity and partial straightening could decrease the formation of entanglements caused by knotting and hooking between the fibers, affecting the yield stress of the suspension.

**Figure 7** presents the results of steady shear experiments under magnetic field with consistencies of 1.0 wt% and 2.0 wt%. The apparent viscosity exhibits a decrease with increasing shear rate, which indicates a shear-thinning behavior. As was mentioned previously, this behavior is related with the rupture of fiber networks and flocs by the imposed shear, rather than the alignment of fibers along the shear flow. In comparison with the results shown in Fig. 5, the suspension consistency appears to not have a significant effect on apparent viscosity in absence of a magnetic field. This can be due to the fact that the higher viscosity of the glycerol-in-water mixture used as a suspending medium masks the effect of fiber concentration.

On the other hand, regarding the effect of the magnetic field, it is observed that in the presence of a magnetic field, the resulting apparent viscosity decreases. This result is contrary to what has been reported for suspensions of cellulose nanowhiskers (rodlike nanoparticles of crystalline cellulose), where as a consequence of the diamagnetic susceptibility of cellulose [42], the magnetic field hinders the nanoparticles' alignment along the flow field direction, exhibiting an increase in shear viscosity in the suspension [43]. Likewise, experiments performed on suspensions of cobalt microfibers [21] have shown that under the action of a magnetic field, friction between particles increases due to attractive magnetic forces, leading the suspension to a higher resistance to flow and exhibiting viscoplastic behavior.

However, because the material used for our experiments consisted of long fibers having twists and blends, the complete orientation of fibers along the magnetic field is difficult. Thus, the reduction of the viscosity can be explained by the same reasons exposed previously for yield stress. Although at too low consistencies it is possible to significantly improve the magnetic alignment [20], at higher consistencies, the bulky structures formed hinder the free rotation of fibers, so the reduction of inter-fiber interactions by the rigidity of the fibers allows the shear forces to disrupt flocs more easily. This effect of fiber flexibility on apparent viscosity was experimentally demonstrated by Keshtkar et al. [36] using fiber-model suspensions. Additionally, weak attractive magnetic forces between magnetic fibers might provoke a floc size reduction, decreasing the volume fraction of flocs in the suspension. Hence, the combination of both effects could be the cause of the lower viscosity observed when the magnetic field is applied.

Finally, the Cross model (Eq. 3) was fitted to experimental apparent viscosity data:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\lambda \dot{\gamma})^a} \quad (3)$$

where the constants  $\eta_{\infty}$ ,  $\eta_0$ ,  $\lambda$ , and  $a$  have the same meaning as in Eq. 2. It is observed in Fig. 7 that the Cross model well fits the experimental data, and the obtained fitting parameters are summarized in **Table II**. Values of the Cross model constants indicate a lower shear rate for the onset of shear thinning when the magnetic fiber suspensions are in presence of the external magnetic field, as given by the reciprocal of the time constant,  $1/\lambda$ . Additionally, constant  $a$  shows less dependency of apparent viscosity on shear rate when the magnetic field is applied. Thus, under the action of a magnetic field, the magnetic fiber suspension thins earlier and its viscosity response is less affected by changes in shear rate, probably due to the fact that flocs in the suspension are looser and smaller than with the absence of an external magnetic field. This is a

| $C_m$ ,<br>wt% | $H$ ,<br>G | $\eta_{\infty}$ ,<br>Pa·s | $\eta_0$ ,<br>Pa·s    | $\lambda$ ,<br>s      | $a$  |
|----------------|------------|---------------------------|-----------------------|-----------------------|------|
| 1.0            | 0          | 2.24                      | 36.21                 | 7.91                  | 1.81 |
|                | 2100       | 1.18                      | *1.08×10 <sup>6</sup> | *7.97×10 <sup>5</sup> | 1.07 |
| 2.0            | 0          | 1.84                      | 108.65                | 23.93                 | 1.19 |
|                | 2100       | 0.66                      | 105.66                | 54.60                 | 0.97 |

$C_m$  = suspension mass consistency;  $H$  = magnetic field strength;  $\eta_{\infty}$  = infinite-shear viscosity;  $\eta_0$  = zero-shear viscosity;  $\lambda$  = time constant;  $a$  = constant indicating transition to the decreasing portion of the viscosity; and  $n$  = power-law-like index.

\*These unexpectedly high values are due to the data range analyzed, where it is observed that a monotonic increase of the viscosity as the shear rate tends to zero.

## II. Parameters of the Cross model for suspensions of magnetic fibers/glycerol in the presence of an external magnetic field.

consequence of the lower energy required to break flocs because of the stiffness of fibers, as previously mentioned.

It is well known that, for a fiber suspension, there exists a depletion layer near the shearing walls from which fibers are excluded [2,44]. The overall strain is localized in this lower-viscosity layer, so to prevent the occurrence of wall slippage, it is recommended to use geometries with rough surfaces [45]. Thus, Swering et al. [41] and Damani et al. [46] measured the yield stress of non-magnetic pulp suspensions using a roughened parallel plate geometry. Likewise, Oleksandr et al. [47] used a serrated cone-and-plate geometry to show that microfibrillated cellulose suspensions exhibit higher viscosities at low shear rates compared with a smooth surface. These observations are an indication that wall slip has a great effect on measurements, so the values obtained for yield stress and apparent viscosity in our magnetorheological measurements are probably lower than those of the actual suspension. However, the results obtained in this study show a clear tendency of the rheological properties of magnetic fiber suspensions, whether in the presence of a magnetic field or not.

## CONCLUSIONS

Magnetic fiber suspensions are of great interest due to their potential applications in the production of paper sheets for valuable documents such as bank checks, identity cards, passports, security papers, etc. In this research, the rheological and magnetorheological properties of magnetic fiber suspensions were studied at different conditions of consistency and temperature. Suspensions were prepared from eucalyptus fibers modified with cobalt ferrite nanoparticles by the lumen loading method, and a rotational rheometer was used for rheological measurements.

From SEM images, it was observed that nanoparticle agglomerates were deposited on the surface and into macropores of fibers; also, magnetic characterization showed the ferromagnetic behavior of the magnetic fibers and nanoparticles. In absence of an external magnetic field, rheological measurements showed that the yield stress increased with increasing the consistency of the suspension, as well as with the concentration of magnetic fibers. Additionally, the yield stress was relatively unaffected by temperature when it increased from 25°C to 50°C. On the other hand, in shear flow tests, all the suspensions exhibited non-Newtonian “shear-thinning” behavior, where the apparent viscosity increased with the consistency of the suspension independently of the concentration of magnetic fibers. The Carreau-Yasuda model was successfully used to fit the apparent viscosity data.

Finally, magnetorheological measurements showed that both the yield stress and apparent viscosity decrease under the action of an external magnetic field, which was attributed to the stiffness and partial straightening of magnetic fibers when these tend to align along the magnetic field

applied. The use of a roughened surface is recommended to prevent the formation of a depletion layer on shearing walls. **TJ**

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## ABOUT THE AUTHORS

Since cellulose is a renewable natural material, there has been growing interest in research related to cellulose-based composites. The incorporation of magnetic particles gives fibers the capability to respond to an external magnetic field, making them a very useful material for different applications.

In this study, we focused on the rheology of magnetic pulp suspensions and the effect of a magnetic field on it. We found that magnetic particles are deposited as aggregates onto the surface and into macropores of the fibers, leading the magnetic fibers to a ferromagnetic behavior. Furthermore, in the absence of a magnetic field, yield stress of suspensions increases with the concentration of magnetic fibers, whereas apparent viscosity is unaffected. On the other hand, yield stress and apparent viscosity of suspensions decrease under the action of an external magnetic field.

Those who work in the field of the rheology of suspensions, especially for those who transform natural fibers into value-added products, will find these results useful for their application in areas such as



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nanotechnology and production of special papers. Our next step is to study the effect of the application of a magnetic field in the formation stage on the mechanical properties of magnetic papers.

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