Optimization of the Percentage of Cellulose, Latex and Metakaolin in the Production of Cementitious Composites

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Abstract – In this work the influence of the addition of the variables cellulose kraft pulps, natural rubber latex and metakaolin as reinforcements in cementitious composites was studied. The influence of the analyzed variables on the properties of the cementitious composites was evaluated through an experimental design (DOE) at 28 days age. The best modulus of rupture was the 12.29 MPa presented by the composite with 7.097% cellulose, 0.37% latex and 50.155% metakaolin. The composite with 5.928% cellulose, 1.85% latex, and 55.195% metakaolin had the best toughness of approximately 1.10 kJ/m². According to the results obtained contact angle, it was possible to prove that the latex adhered to the pulp, hydrophobizing it. Therefore, it was concluded that it is possible to use the natural rubber latex in the cellulosic pulp and the metakaolin to protect the fiber in cementitious composites.

Keywords – Cellulose kraft pulp, Design of experiments, Flexural strength, Natural rubber latex.

I. INTRODUCTION

One of the main problems of the civil construction is the generation of waste, the scarcity of natural resources, the energy consumption, the gases emission, that is, the impact caused to the environment. According to [1], the 20% of global CO₂ emissions related to industry, the cement industry accounts for approximately a quarter of total emissions. In this sense, research is being carried out with the objective of reducing environmental impact by use renewable materials. The natural fibers deserve special attention because they present interesting properties, such as good mechanical in fragile matrices, ductility, stiffness, low density, toughness, high availability, have a renewable source and low production cost [2,3,4,5].

Although the advantages presented, studies have shown limitations on the use of natural fibers as reinforcement in cementitious matrices. The alkalinity of the cement paste deteriorates the fiber by the lignin, hemicelluloses and the amorphous part of cellulose degradation and solubilization, reducing mechanical performance of the fiber and, consequently, the durability of the composite. This occurs because the presence of hydroxyl groups in the celluloses structure, characterizing their polar and hydrophilic nature, increases the water absorption that facilitates alkaline attack and causes dimensional instability. In addition, the precipitation of cement hydration products, mainly calcium hydroxide (CH), in the lumen of the natural fibers resulting in their embrittlement by a process called mineralization [5,6,7].

The treatment of natural fibers are the focus of several researches, or even matrix, to enable their use. Among the treatments is the reduction of the alkalinity of the matrix by replacing part of the cement with pozzolanic materials, the chemical treatment of the fibers and the physical treatments of the fiber (thermomechanical treatments and the physical modification of the fibers) [8,9,10,11,12].

The natural rubber latex (NRL) in a stable state with ammonia is a natural polymer often used in cement composites. [13] reported in their study that latex forms a film in the voids, pores and micro cracks of the composites that provides greater adhesion between the fiber and matrix, reducing its permeability. Thus, there is reduction of chemical attacks increasing the durability of composites.[14] observed a reduction in water absorption in cement composites with the addition of approximately 2.5% NRL.

Hemp fibers were studied with the application of a latex coating (NRL) to improve durability and mechanical properties of composites [15]. According to the authors, the latex coating improved the durability of hemp fiber in the pozzolanic mortar mix, with improved bonding between the fiber and the mixing. In this way, the mechanical properties were increased, providing a considerable durability to the composites.
The NRL is an alternative between the materials used in the modification of the composites, for being of a renewable source and has a hydrophobic character. The hydrophobicity of the latex possibly protects the fiber physically against the degradation caused by the alkaline water contained in the pores of the pulp. Moreover, the use of latex as a composite addition enables improvements in their properties, for example in porosity reduction and water absorption, as previously mentioned [13,17]. The aim of the present work was study the influence of parameters like cellulose kraft pulps, natural rubber latex and metakaolin as reinforcements in cementitious composites.

II. MATERIALS AND METHODS

2.1 Characteristics of materials

2.1.1 Cellulose kraft pulp, cement, latex and metakaolin

The composites were molded using cellulose, with the specific mass of 1.5 g/cm³, extracted from Eucalyptus urograndis, processed industrially by the Kraft method, and supplied by Suzano (Limeira/SP). The bleached kraft sheets were cut in smaller pieces and dispersed in water by mechanical shaking. They were filtered to remove excess water. The pulps were stored in plastic bags under refrigeration. The cement used was the Ultra Fast - CPV ARI, of the Holcim brand. The manufacturer supplied the properties of the cement. Farm Varginha, located in Araguari, provided Minas Gerais natural rubber latex, extracted from the rubber tree (Hevea brasiliensis). The latex was stabilized with an ammonium hydroxide solution (NH₃OH) in the proportion of 50 mL of NH₃OH solution to 5 L of latex. Part of the cement used in the composites was replaced by Metacaulim HP ULTRA, provided by Metacaulim do BrasilIndústria e ComércioLtda (Jundiaí-SP). This product consists of SiO₂ and Al₂O₃ in the amorphous phase [17].

2.2 Materials characterization

2.2.1 Cellulose and composites characterization

2.2.1.1 X-ray diffraction analysis (XRD)

The cellulose fibers were submitted to X-ray diffraction analysis to identify their characteristics peaks presented in 2θ between 10° and 90°. This study was carried out at the Multiuser Laboratory of the Institute of Chemistry of the Federal University of Uberlândia (IQ/UFU). A Shimadzu diffractometer, model XRD-6000, with CuKα radiation (1.540 Å), voltage of 40 kV and current of 30 mA was used. As for the composites of the experiments, they were transformed into powder and later they were sifted in a sieve with 75 µm opening.

2.2.1.2 Scanning electron microscopy (SEM)

The samples were cut in the dimensions of 1 cm x 1 cm and placed in an oven at 50 ± 1 °C for 24 hours. The composites of the experiments were investigated with the objective of analysing their surface microstructure, the presence of pores, the fiber-matrix interface, and the distribution of cellulose and latex in the pulp (1 cm x 1 cm in size). The analyses were carried out using the microscope model Vega3, brand TESCAN, located in the Laboratory of Multiusers of the Institute of Chemistry of UFU (IQ/UFU). Gold was used at a voltage of 5 kV to metallize the fibers.

2.2.1.3 Contact angle analysis

Contact angle measurements were performed using a contact angle equipment of Theta Lite Optical Tensiometer, model TL100, with 60 frames per second CCD, located in Laboratory 06 of the Federal University of the TriânguloMineiro (UFTM), Univerdecidade II campus, Uberaba/MG. A syringe type Hamilton, 100 microliters of capacity with a volume drop of 5 microliters. The contact angle was used to evaluate the surface energy of cellulose and of the cellulose with latex molded by the Hatschek method. The solvent used to measure the contact angles was deionized water.

2.2.2 Cement, latex and metakaolin characterization

The cement, latex and metakaolin were analyzed by X-ray diffraction to determine its characteristic peaks. The analysis were performed in the same apparatus and for the same configurations used for cellulose. The SEM analyses of latex were performed in the same apparatus and for the same configurations used for cellulose. For that, removed the moisture from the investigated samples, in an oven, at 45 ± 1 °C for 24 h [16]. For the sample whose cross section of the latex was evaluated, the integrity of the cross-sectional structure was insured by immersing the sample in liquid nitrogen and fracturing it using a tweezer. The mechanical properties of the latex were evaluated by direct tensile test, using the Instron brand machine, model 5982, with a 5 kN load cell was used. This test was performed according to the parameters used by [18] for determination of plastic tension. By this test, it was possible to determine the tensile strength, maximum deformation and Young’s modulus characteristic of latex. The Instron brand test machine, model 5982, with a 5 kN load cell was used for the test. The chemical, physical and mechanical analysis of the cement was performed by the Lafarge Holcim manufacturer.

The chemical composition, granulometric composition, physical properties and pozzolanic activity of metakaolin were obtained through the material data sheet provided by Metacaulim do Brasil [17] on its website. The Materials and Structures Laboratory of the Federal University of Paraná (UFPR) made the analysis of the chemical composition.
The mechanical and chemical properties of composites were studied according to a statistical process [22], which means that the stationary point (\(\lambda_i\)) of the characteristic roots \(\lambda_i\) is a point of minimum. If \(\lambda_i > 0\), the stationary point is a point of maximum. In contrast, if \(\lambda_i < 0\), a move in any direction from the stationary results in a decrease in \(\hat{y}\), which means that the stationary point is a point of maximum. In contrast, if \(\lambda_i > 0\), the stationary point is a point of minimum. If \(\lambda_i\) have a different signal, the stationary point represents a saddle point. In this work, the canonical analysis was implemented using the software Maple 17.

The mixing and preparation of the composites were carried out using the principle of the Hatschek process developed by the software Statistica12. The studied response variables were fitted in a quadratic model using linear regression analysis and p-value less than 0.10 (p < 0.10) were considered statistically significant. The coded variables were determined by equations 1, 2 and 3:

\[
X_1 = \frac{(\text{Cel}(\%) - 5.0)}{3.5}
\]

\[
X_2 = \frac{(\text{Lat}(\%) - 0.115)}{0.095}
\]

\[
X_3 = \frac{(\text{Mk}(\%)) - 19)}{15}
\]

Where Cel, Lat e Mk are coded variables of percentage of cellulose, latex, and metakaolin, respectively.

Table.1: Coded and uncoded levels of variables used for central composite design.

| Parameters      | Symbol  | Uncoded | Coded   | -1.414 | -1   | 0   | +1    | +1.414 |
|-----------------|---------|---------|---------|--------|------|-----|-------|--------|
| Cellulose (%)   | Cel     | X_{Cel} | (X_1)   | 0.05   | 1.5  | 5.0 | 8.5   | 9.95   |
| Latex (NRL) (%) | Lat     | X_{Lat} | (X_2)   | 0      | 0.02 | 0.115 | 0.21  | 0.249  |
| Metakaolin (%)  | Mk      | X_{Mk}  | (X_3)   | 0      | 4.0  | 19  | 34    | 40     |

2.3.1 Optimization
The nature of the stationary point was determined by canonical analysis. This technique consists of a translation of the origin of the response surface \((x_1, x_2, x_3, ..., x_k) = (0,0, ..., 0)\) for the stationary point. Consequently, the canonical form of the adjusted surface is written as a function of new variables \((w_1, w_2, w_3, ..., w_k)\), whose axes correspond to those of the main system contours. The optimal conditions of percentage of cellulose (%Cel), percentage of latex (%Lat) and percentage of metakaolin (%Mk) for the variables responses were determined by canonical analysis. Equation 4 represented the function in terms of these new variables [19].

\[
\hat{y} = \hat{y}_0 + \hat{A}_1 w_1^2 + \hat{A}_2 w_2^2 + ... + \hat{A}_n w_n^2
\]

After the translation of the response surface into the canonical form, the signal and magnitude of the stationary point of the characteristic roots \(\lambda_i\) can determine the nature of the stationary point. Therefore, if \(\lambda_i < 0\), a move in any direction from the stationary results in a decrease in \(\hat{y}\), which means that the stationary point is a point of maximum. In contrast, if \(\lambda_i > 0\), the stationary point is a point of minimum. If \(\lambda_i\) have a different signal, the stationary point represents a saddle point. In this work, the canonical analysis was implemented using the software Maple 17.

2.4 Composites preparation
The mixing and preparation of the composites were carried out using the principle of the Hatschek process [20]. Initially, the cellulose was incorporated into the water, followed by latex, cement and metakaolin. To each material added to the mixer, the mixture was stirred for 5 min until its complete homogenization. The mass solids concentration, for each composite, was 40%. The specimens had dimensions of 20 cm x 20 cm the side and 4 mm in thickness.

2.5 Composites characterization
2.5.1 Flexural strength test
Flexural tests was performed at 28 days of age. The rupture test method used was the four-point flexural test recommended by [21], in which the load application is done in two points of the sample, generating a constant moment between the points of load, using a Universal Machine of Instron brand tests, model 5982, and load cell of 5 kN. The distance between the lower supports was 150 mm and the load application speed was 2 mm/min.

III. RESULTS AND DISCUSSION
3.1 Characteristics of materials
3.1.1 Cellulose kraft pulp, cement, latex and metakaolin
The composites were molded using cellulose, with the specific mass of 1.5 g/cm³, extracted from Eucalyptus urograndis. In the process of obtaining the cellulose pulp, a solids content of 13.33% [22] was obtained after the filtration step. The mechanical and chemical properties of Portland cement CPV ARI presented values according to the requirements of ABNT NBR 16697:2018.
rubber latex with a solids content of 43.33% by weight was obtained after drying the emulsion according to [16]. According to with the chemical characterization of metakaolin, it presents expressive percentages of SiO\textsubscript{2} (51.57%) and Al\textsubscript{2}O\textsubscript{3} (40.5%), making approximately 92% of these two compounds. It also has small amounts of Fe\textsubscript{2}O\textsubscript{3} (2.8%), Na\textsubscript{2}O and K\textsubscript{2}O (< 1%) [17].

3.2 Materials characterization

3.2.1 Cellulose characterization

3.2.1.1 X-ray diffraction analysis (XRD)

The diffractogram of the bleached cellulose kraft pulp is shown in Fig. 1a. Two diffraction peaks characteristic of cellulose were observed. The first peak occurred in 2θ between 18º and 19º, while the second corresponded to 2θ between 22º and 23º, both of the type I polymorph of native cellulose [23].

3.2.1.2 Scanning electron microscopy (SEM)

3.2.1.3 Contact angle analysis

This analysis was done for the first value of the contact angle after stabilization of the water drop on the surface of the sample. The contact angle of the samples with latex addition (CLH) had a contact angle (\(a\)) of 92.56º compared to 73.89º for pure cellulose. The pure cellulose presented a rapid dispersion of the water droplets and, consequently, a contact angle of less than 90º, that is, the sample surface is extremely hydrophilic, while the samples with latex addition (CLH) had contact angles higher than 90º, which implies that the latex hydrophobized the sample eventually. This occurred because the latex possibly forms a film that protects the fiber, occupying partially the empty spaces and, consequently, occurring its hydrophobization [26,27].

3.2.2 Cement, latex and metakaolin characterization

Fig.2a shows the diffractograms of the CPV ARI cement. It was possible to prove the presence of the main constituents of the CPV ARI cement, such as tricalcium silicate (C\textsubscript{3}S) and dicalcium silicate (C\textsubscript{2}S), whose most prominent diffraction peaks are coincident because they have similar chemical composition. These coincident peaks presented values of 2θ equal to 29.5º, 32.3º, 33.3º, 34.4º and 41.3º (ICSD 64759 and ICSD 963). The tricalcium silicate also showed values of 2θ at 30.1º, 38.8º,
Fig. 2. XRD patterns: a) CPV ARI cement; b) Metakaolin; c) Latex (NRL).

Figs. 2b e 2c show metakaolin and latex (NRL) diffractograms, respectively. According to Fig. 2b, it was possible to prove the presence of the main constituents of metakaolin, such as quartz (SiO$_2$), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), muscovite (KAl$_2$(Si$_3$AlO$_10$)(OH)$_2$) and hematite (Fe$_2$O$_3$). The quartz showed peaks in values of 2θ equal to 21º, 25.3º, 26.6º, 42.5º, 50º, 59.9º and 68.2º (ICSD 89281). The kaolinite peaks were at 21 °, 27.1 °, 36.5 °, 39.4 °, 45.9 °, 50 °, 54.7 ° and 67.7 ° (ICSD 80082), among others, and possibly indicate that the clay did not suffer total calcinations [29].

In addition to the XRD characterization, it is important to note that the metakaolin is a material of great pozzolanic activity because it presents a consumption of 771.2 mg of CaO/g of sample, obtained through the Modified Chapelle method. The limit for considering a material as low reactivity is 330 mg of CaO/g of sample [17]. According to Fig. 2c, the NRL is an amorphous polymer having a typical diffractogram of this type of material. It presents a wide spreading shoulder centered at 2θ equal to 19º, attributed to the amorphous regions of the sample and absence of crystalline peaks. [28,29] reported similar results in their studies. In addition, according to the SEM analysis, it was observed that the latex sample presented a continuous, smooth matrix with the homogeneous surface along the length. Fig. 3 shows the stress curves versus deformation for the seven tensile test NRL specimens. It can be concluded that the latex has a low tensile strength and great deformability (ductile) with deformations above 300%. These characteristics are typical of an elastomeric material (Callister, 2000). The NRL specimens had low
Young’s modulus and tensile strength, with a mean of 0.64 and 0.19 MPa, respectively.

Table 2. The experimental conditions studied in CCD matrix, with uncoded values of parameters.

| E* | Cel (%) | Lat (%) | Mk (%) | MOR (MPa)** | T (kJ/m²)*** |
|----|---------|---------|--------|-------------|--------------|
| 1  | 1.5     | 0.02    | 4      | 9.11        | 0.08         |
| 2  | 1.5     | 0.02    | 34     | 8.85        | 0.1          |
| 3  | 1.5     | 0.21    | 4      | 7.23        | 0.07         |
| 4  | 1.5     | 0.21    | 34     | 8.78        | 0.11         |
| 5  | 8.5     | 0.02    | 4      | 9.1        | 1.12         |
| 6  | 8.5     | 0.02    | 34     | 7.29        | 1.03         |
| 7  | 8.5     | 0.21    | 4      | 13.26       | 1.69         |
| 8  | 8.5     | 0.21    | 34     | 14.42       | 1.68         |
| 9  | 0.05    | 0.115   | 19     | 6.75        | 0.04         |
| 10 | 9.95    | 0.115   | 19     | 4.54        | 0.68         |
| 11 | 5.0     | 0       | 19     | 10.29       | 0.5          |
| 12 | 5.0     | 0.249   | 19     | 13.73       | 0.48         |
| 13 | 5.0     | 0.115   | 0      | 10.91       | 0.29         |
| 14 | 5.0     | 0.115   | 40     | 12.57       | 0.52         |
| 15 | 5.0     | 0.115   | 19     | 11.42       | 0.45         |
| 16 | 5.0     | 0.115   | 19     | 12.47       | 0.47         |
| 17 | 5.0     | 0.115   | 19     | 9.03        | 0.37         |
| 18 | 5.0     | 0.115   | 19     | 10.93       | 0.47         |

*E: Experiment; **MOR: Modulus of rupture; ***T: Toughness.

3.3 Design of experiments (DOE)
3.3.1 Global statistical analysis - effect of independent variables
Table 2 shows the values of the response variables (modulus of rupture and toughness) for the 18 experiments of the experimental design obtained by the flexural tests.

3.3.1.1 Modulus of rupture
The empirical equation that represents the variation of the modulus of rupture in function of the independent variables was obtained by multiple regression, resulting in equation 5. Each parameter has a significance analyzed according to the probability value ($p$-value).

This value tests the null hypothesis that the coefficient obtained for the variable is equal to zero, without effect. Thus, a $p$-value below 0.10 ($p < 0.10$) indicates that the null hypothesis can be rejected and that the variable correlates with the response.

\[
\text{MOR(MPa)} = 11.69 - 2.48(X_{Cel})^2 + 1.18(X_{Lat}) + 1.65(X_{Cel})(X_{Lat})
\]  

(5)

Where, MOR is the modulus of rupture.

The quadratic term of percentage of cellulose ($X_{Cel}$), the linear variable of the percentage of latex ($X_{Lat}$) and the interaction between both ($X_{Cel}X_{Lat}$) was significant for the modulus of rupture. The value of $R^2$ of equation 5 was 0.72, that is, the equation significantly represented the modulus of rupture to a confidence level of 90%.

Fig. 4 shows the response surfaces for the modulus of rupture. According to Figs. 4a and 4b, with values of metakaolin and latex at the center point, it has been found that there is a maximum value for the modulus of rupture when the amount of cellulose is close to the coded value of 0.5 (approximately 6.75% cellulose in the composite). The increase in the modulus of rupture to cellulose intermediate values possibly proves that, for approximately 6.75% of cellulose in the composite, there is a reduction of cracking and an increase of the performance due to the homogeneous dispersion and fibers adhesion on the matrix. Possibly, for lower quantities, there is a reduction in the modulus of rupture by the insufficient amount of fibers and, for higher quantities, due to the loss dispersion caused by a large amount of fiber. This same trend was observed in studies conducted by [31].
Fig. 3. Stress vs. deformation for the seven samples of the natural latex emulsion.

According to Figs. 4a ($X_{Mk} = 0$) and 4c ($X_{Cel} = 0$) observed that there was an increase in the modulus of rupture for larger amounts of latex in the mixture. [26] also observed an increase in the resistant capacity and attributed this fact to the greater amount of pozzolan adhered to the fibers surface that may have caused a local pozzolanic effect in the fiber-matrix interface. The pozzolanic reaction consumes portlandite and produces hydrated silicates and calcium aluminates that lower local pH and increase the strength and cohesion of the composites. Finally, by the Figs. 4b ($X_{Lat} = 0$) and 4c ($X_{Cel} = 0$), it was observed that the amount of metakaolin does not significantly interfered in the modulus of rupture within the intervals studied.

3.3.1.2 Toughness
The equation 6 represents the variation of the toughness in function of the independent variables, obtained by multiple regression.

$$T (kJ / m^2) = 0.56 + 0.51 (X_{Cel})$$

(6)

Where, $T$ is the toughness.

According to equation 6, only the linear variable of the percentage of cellulose ($X_{Cel}$) was significant for the toughness, representing significantly the toughness for a 90% confidence level, because there was a dispersion of the data and the composites may present differences in their values ($R^2 = 0.70$). Fig. 5 shows the response surfaces for the toughness.

Observing the Figs. 5a ($X_{Mk} = 0$) and 5b ($X_{Lat} = 0$), it was observed that the highest toughness values are obtained when the cellulose percentage in the mixture increased, independent of the concentrations of latex and metakaolin. This may be possibly explained by greater control of cracks propagation. The higher values of toughness could possibly indicate a fracture of the composite by pull out fiber due to the higher energy consumption [32].

3.3.2 Optimization
3.3.2.1 Optimization and canonical analysis for the modulus of rupture
In order to analyze the response surfaces and perform optimization of the response variables was done the canonical analysis. Thus, response functions of the modulus of rupture were expressed in terms of new variables (canonical) $w_1$, $w_2$, and $w_3$, and are given by equation 7, for the modulus of rupture.

$$f = 10.38 - 2.69 w_1^2 + 0.44 w_2^2 + 1.05 w_3^2$$

(7)

According to the resulting values for the roots of the equation $\lambda_1$, $\lambda_2$ and $\lambda_3$, the stationary point is a saddle point of the adjusted surface because the roots presented different signals ($\lambda_1$ was negative and, $\lambda_2$ and $\lambda_3$ were positive). The values obtained for the stationary point of $X_f$
Fig. 4. Response surface of the modulus of rupture: (a) % metakaolin at the central level (X_3 = 0); (b) % latex at the central level (X_2 = 0); (c) % of cellulose at the central level (X_1 = 0).

(%cellulose), X_2 (%latex), and X_3 (%metakaolin) were equal to -0.137, -0.740, and 0.141, respectively, and within the experimental region. That is, they did not exceed the values of +\( \alpha \) (+1.41421) and -\( \alpha \) (-1.41421). These values for the variables \( X_1, X_2, \) and \( X_3 \) are physically possible to be applied to the mixture, as they result in positive percentages of cellulose, latex, and metakaolin.

Analyzing the coding equation of each variable (equations 1, 2 and 3), the restrictions, for percentage of cellulose, latex and metakaolin were, respectively: \( X_1 \geq -1.429, X_2 \geq -1.211 \) and \( X_3 \geq -1.267 \). Once, \( X_1 \leq -1.429, X_2 \leq -1.211 \) and \( X_3 \leq -1.267 \) result in physically impossible values, that is, negative amounts of the reagents. By studying the adjusted surface in the canonical form for the modulus of rupture, it was concluded that the response increases in the direction \( w_2 \) and \( w_3 \) and decreases in the direction of \( w_1 \). As the objective of the analysis is to increase the value of the modulus of rupture, it was chosen to vary the \( w_3 \) values because it has a greater influence on the response than \( w_2 \) because it has a higher coefficient.
(λ₁ = 1.050 and λ₂ = 0.435), and values that resulted in zero for w₁ (negative root) and w₂. It was possible to relate the canonical variables with the three independent variables (X₁, X₂, and X₃), according to equation 8.

\[ w = M'(X - X₀) \]  \hspace{1cm} (8)

Developing the equation 8, it was obtained the following recurrence equations:

\[
\begin{bmatrix}
W₁ \\
W₂ \\
W₃
\end{bmatrix} =
\begin{bmatrix}
0.3987X₁ - 6.7792 - 0.9014X₂ - 0.1690X₃ \\
-0.3338X₁ + 1.9165 - 0.3143X₂ + 0.8887X₃ \\
0.8542X₁ - 2.7682 + 0.2979X₂ + 0.4262X₃
\end{bmatrix}
\]

With conditions found for X₁, X₂, and X₃ and applying the value of zero for w₁ and w₂, the various values of w₃ obtained are listed in Table 3. By analyzing the values listed in Table 3, for values of w₃ ≤ -1.0, it can be concluded that the values for X₃ are physically impossible, resulting in negative amounts of the latex according to the restrictions imposed by the coding equations (X₂ ≥ -1.211).

Therefore, the most appropriate condition, according to acceptable composites characteristics, which optimizes the modulus of rupture, was w₃ = 4.0, where:

\[ X₁ = 0.599, \quad X₂ = 2.682 \quad \text{and} \quad X₃ = 2.077 \]  \hspace{1cm} \text{(only X₁ is within the studied range).}

For this optimized condition where w₃ = 4.0, the percentage of cellulose is 7.097% (within the range studied), latex is 0.370% (outside the range studied) and metakaolin is 50.155% (outside of range studied), resulting in a modulus of rupture of 27.190 MPa. However, it was observed that there are higher optimization results for the modulus of rupture, but for a very large amount of metakaolin in relation to the amount of cement, that, possibly, would generate insufficient hydration products (calcium hydroxide) to be consumed by metakaolin.

By the study of the response surfaces, the maximum value for the modulus of rupture was approximately 14 MPa as shown in Fig. 4a. Through the optimization, it was possible to find a modulus of rupture of 27.190 MPa, for a variable within the studied range \((X₁ = 0.599)\). The value experimental obtained was 12.29 MPa. It can be seen that the results were very coherent with respect to the optimization property, that is, the composite to obtain the major modulus of rupture was the one that presented the highest value of MOR among the optimal composites. The optimal value experimental obtained were much lower when compared with the value obtained in the

\[(\lambda₁ = 1.050 \quad \text{and} \quad \lambda₂ = 0.435), \quad \text{and values that resulted in zero for w₁ (negative root) and w₂. It was possible to relate the canonical variables with the three independent variables (X₁, X₂, and X₃), according to equation 8.}\]
optimization, as was expected, once was much higher than that found in the literature.

3.3.2.2 Optimization and canonical analysis for the toughness

The equation 9 represents the surface adjusted for the calculation of the toughness in function of new canonical variables (w1, w2, and w3).

\[
\tilde{y} = -1.44 + 0.018w_1^2 + 0.09w_2^2 + 0.186w_3^2 \quad (9)
\]

Given the results of the values for the roots of the equation, λ1, λ2, and λ3 (all roots were positive), the adjusted surface has a minimum point. Still, any movement in directions of w1, w2, and w3 will increase the toughness. For the stationary point, it was observed that only the value of X1 (% metakaolin) was within the experimental region (X1=0.518). The value of variable X1 (-8.819) is physically impossible because the amount of cellulose in the mixture would be negative (uncoded cellulose value equal to -25.867%). The toughness increases in all directions (w1, w2, and w3), and in order to maximize the response, the values of w3 were varied, because it had the largest coefficient, with the highest influence on the final response, determining conditions of X1, X2, and X3 that zero the values of w1 and w2.

The canonical variables were related to the three independent variables (X1, X2, and X3), according to equation 8. Developing this equation, obtained the following recurrence equations:

\[
\begin{bmatrix}
W_1 \\
W_2 \\
W_3
\end{bmatrix}
= 
\begin{bmatrix}
0.8348X_1 + 9.9208 - 0.5464X_2 - 0.06745X_3 \\
0.0063X_1 - 0.0403 + 0.1318X_2 - 0.9913X_3 \\
0.5505X_1 + 0.9772 + 0.0271X_2 + 0.1134X_3
\end{bmatrix}
\]

Based on the recurrence equations, the conditions found for X1, X2, and X3 and applying the value of zero for w1 and w2, the various values of w3 obtained were listed in Table 4.

According to Table 4, for values of w3 ≤ 10, the values of X1 are physically impossible, because, by the restrictions imposed, it must be greater than -1.429. Therefore, in order not to extrapolate the limits of the constituents adopted, the condition chosen was w3 = 16.5, where: X1 = 0.264 (within the studied range), X2 = 18.265, and X3 = 2.413. For this optimized condition, in the decoded values, 5.928% of cellulose, 1.850% of latex and 55.195% of metakaolin were obtained, resulting in a toughness of 48.921 kJ/m². It was possible to achieve higher values for toughness. However, it would be necessary to replace large quantities of cement with metakaolin, which would be impracticable due to the insufficient production of calcium hydroxide to be consumed by metakaolin. The value experimental obtained was 1.08 kJ/m². The optimal value experimental obtained were much lower when compared with the value obtained in the optimization, as was expected, once was much higher than that found in the literature. As was found for the modulus of rupture, the best result found for the toughness by analyzing the response surfaces was the formulation of experiment 8 (8.5% cellulose, 0.21% latex, and 34% metakaolin). This condition resulted in an approximate value of 1.6 kJ/m².

3.4 Composites characterization

3.4.1 X-ray diffraction analysis (XRD)

Fig.6 shows the normalized XRD diffractograms of the composites. The ettringite (3CaO.A12O3.3CaSO4.32H2O), the hydrated calcium silicate (C-S-H), the portlandite (Ca(OH)2), the calcite (CaCO3) and the quartz (SiO2) were the main hydrated compounds identified. It was possible to verify the presence of ettringite in the composites whose main peaks were 20 equal to 26.3º, 32.7º and 41.4º.
The portlandite identification indicates that there is remaining lime even after 28 days of age. The presence of calcium hydroxide is essential for the determination of metakaolin reactivity, because, possible, it is responsible for the portlandite consumption in the pozzolanic reactions.

![Normalized XRD diffractograms of composites: a) E1, E2, E3; b) E4, E5, E6; c) E7, E8, E9; d) E10, E11, E12; e) E13, E14, E15; f) E16, E17, E18.]

Thus, analysing the main characteristic portlandite peaks in 2θ equal to 18°, 34.2° and 47.7° (ICSD 15471), it was observed that the higher the amount of metakaolin in the composites, the lower the intensity of the peaks related to the portlandite. There was a significant reduction of calcium hydroxide for a replacement of 40% of the total mass of cement by metakaolin, which possibly decreased the matrix alkalinity. The calcite presence in 2θ equal to 30°, 37°, 44° and 48.4° (ICSD 150) indicates that carbonation reactions may occur during the composites curing period. Still, the calcite can come from the limestone filler that forms the anhydrous cement. Finally, the diffractograms presented the main quartz peak at 2θ...
equal to 26.8º (ICSD 89281), possibly from the crystalline structures of metakaolin that did not participate in the pozzolan reaction. The quartz peak was higher in the composites with higher amounts of metakaolin (%metakaolin ≥ 19%). Some of the main peaks of ettringite, C-S-H, portlandite, calcite and quartz possibly could not be identified due to the small amount present in the composite and/or overlap of the peaks. Similar results were reported by [33,34].

3.4.2 Scanning electron microscopy (SEM)
Fig. 7 shows rupture sections micrographs of the experiments at 28 days of age.

In general, a dense matrix was observed, with few pores and well adhered to the fibers. It was not possible to note the detachment of the fibers in the interface region that would be provided by the volume variation due to the high water absorption. The fibers were preserved intact even for small pulp contents (<2%), experiment 2 (Fig. 7a), for example, these were pull-out during the flexure test. In the experiment 8 (Fig. 7b), it was observed that the fiber fracture mechanism was by extraction and not by rupture, which possibly provided the highest value of toughness found in the flexural strength tests (1.68 kJ/m²) [7,35]. In the analyzed points, a homogeneous dispersion of cellulose pulp was observed in the whole matrix even for composites with high fiber contents, for example, in experiment 10 (Fig. 7c), whose fiber percentage was 9.95%. However, it is not possible to affirm the absence of agglomerations that would eventually damage the composite performance, because the value of the modulus of rupture for these experiments (experiment 10, for example, whose modulus of rupture was 4.54 MPa) was lower when compared to the others. The possible deposition of hydration products on the surface of the fibers was observed.
IV. CONCLUSION

From the results obtained after the flexural tests and their optimization, it was concluded that the use of NRL in cementitious composites, considering the adopted mini-column method, was effective because it allowed a possible polymer impregnation in the vegetal natural fibers, hydrophobizing it. Experimentally, the optimized formulation obtained a toughness of 1.08 kJ/m² with 5.90% cellulose, and in the DOE, the experiment 8 presented the best toughness value (1.68 kJ/m²) with 8.5% cellulose. The best modulus of rupture was the 12.29 MPa presented by the composite with 7.097% cellulose, 0.37% latex and 50.155% metakaolin. Therefore, with the molding method adopted and considering the limits of constituents used, the reinforced composites with cellulose pulp, latex and metakaolin presented a good performance at 28 days of age.

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