RESOL AND NOVOLAC GLYOXAL-PHENOL RESINS: USE AS MATRICES IN BIO-BASED COMPOSITES

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Summary. This study focused on the development of bio-based composites from glyoxal, phenol and sisal fibers. Glyoxal is a dialdehyde obtained from natural sources that is non-toxic and non-volatile. These properties make glyoxal a suitable candidate to replace formaldehyde in the synthesis of phenolic resins. The glyoxal-phenol resins were prepared in both acid medium (novolac-type) and alkaline medium (resol-type). The glyoxal-phenol thermosetting resins were reinforced by sisal fibers (3 cm, 30% w/w). The novolac glyoxal-phenol composite showed improved results for all the tested properties, demonstrating that the acid medium was probably more suitable for the preparation of the glyoxal-phenol resin. The novolac glyoxal-phenol composite showed higher Izod impact strength, higher storage modulus and lower water absorption than the resol glyoxal-phenol composite.

1 INTRODUCTION
The development of composites based on natural components is of great interest for their potential technological applications [1]. The lignocellulosic fibers, such as sisal fibers, can be considered a good option for the reinforcement in biocomposites [2]. The phenolic thermoset polymers are widely known and used because of their excellent properties, such as dimensional and thermal stability and chemical resistance [2]. The phenolic resin can be both resol-type (alkaline catalysis) and novolac-type (acid catalysis). Glyoxal (OHC-CHO) is a dialdehyde that can be obtained from several natural sources, such as the oxidation of lipids, or as a by-product of biological processes. The low vapor tension of aqueous glyoxal solution and its low toxicity are two of the advantages of using glyoxal instead of formaldehyde in the preparation of phenolic resins [1].

2 EXPERIMENTAL
The resol glyoxal-phenol pre-polymer was synthesized by mechanical stirring of phenol, glyoxal solution and potassium hydroxide (1.0:1.6:0.136 mol/mol), at 100°C, for 2 h [1]. The novolac pre-polymer was synthesized by mechanical stirring of phenol, glyoxal (1.0:0.5 mol/mol) and oxalic acid (3.5% w/w relative to glyoxal), at 125°C, for 7 h. The sisal fiber (3 cm, 30% w/w) reinforced composites were obtained by adding the fibers, randomly oriented, to the resin [1]. The composites were characterized as described elsewhere [1].

3 RESULTS AND DISCUSSION
The novolac glyoxal-phenol composite showed higher impact strength (237 ± 16 J m⁻¹) than the resol glyoxal-phenol composite (118 ± 13 J m⁻¹), indicating a better fiber/matrix interaction. The acid medium was probably more suitable for the reaction of the glyoxal,
which is stable in acid solution and is generally stored and commercialized in this type of solution. The SEM images confirmed the better contact at the fiber/matrix interface in the novolac glyoxal-phenol composite (Figure 1a) than in resol glyoxal-phenol composite (Figure 1b). The SEM images of the novolac composite showed that the fibers were more adhered to the matrix after the Izod impact test, and that the fibers were more completely covered by the matrix. Besides, the novolac composite showed a lower number of cracks in the matrix than the resol composite. This observation indicates the lower fragility of this matrix, consistent with the higher value of Izod impact strength of the composite.

![Figure 1](image1.png)

**Figure 1** – (a) Novolac composite SEM images, (b) Resol composite SEM images; (C) Curves of storage modulus (E’) versus temperature; (d) Results of water absorption test.

The novolac glyoxal-phenol composite had a higher storage modulus (E’) and consequently was more rigid than the resol composite (Figure 1c). For composites reinforced with fibers, the value of E’ falls with energy dissipation in the fiber/matrix interface during stress transfer, and a higher dissipation of this energy occurs in composites with a weak interface [1]. In the resol composite the fibers were less adhered to the matrix and the matrix exhibited a higher proportion of cracks (Figure 1b), consistent with the lower storage modulus of this composite. The novolac composite had the lower water absorption (Figure 1d), confirming the better fiber/matrix interface. In the composites reinforced with natural fibers, the fibers are considered responsible for most of the water absorption. Thus, the better coating of the fibers by the matrix in the novolac composite prevented the interaction between water molecules and the fibers, reducing the water absorption in this composite.

4 CONCLUSIONS

Glyoxal demonstrated a potential to replace completely the formaldehyde in the preparation of phenolic resins. The novolac glyoxal-phenol composite showed better results for all the tested properties than the resol glyoxal-phenol composite, demonstrating that the acid medium was more suitable for the preparation of the glyoxal-phenol resin.

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