CHARACTERIZATION OF A PHENOLIC RESIN AND CARIA SPECIES FIBER COMPOSITE[+]

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Abstract

Polymeric materials are increasingly replacing metallic materials as a result of their properties. In this work a composite of phenolic resin and *caria species* fibers and molasses was developed. The molasses has been previously alkalinized. The dough had been dried, milled and the particles classified in a range of grain sizes. Experimental assays were performed, varying the proportion of the resin and the reinforcement and the size of the particles, keeping the pressure and molding temperature constant. These composites were characterized according to physical and mechanical properties. The obtained results clearly indicat the extent of fiber-matrix interface adhesion. Fiber-reinforced composites show variation in their density, water resistance, compressive strength and hardness.

المستخلص

بدأت المواد البوليمرية باستبدال المواد المعدنية بشكل متزايد نتيجة لخواصها. في هذا البحث تم تطوير متراكب من راتنج الفينول مع ألياف خشب الجاوي والمولاس. عومل المولاس في البدء مع قاعدة. جففت العجينة وطحنت والدقائق صنفت وفقا لاحجامها. اجريت التجارب بتغيير نسب الراتنج ومواد التسليح (عجينة الألياف والمولاس) وحجم الدقائق مع الإبقاء على ضغط ودرجة حرارة الصب ثابتة. هذه المركبات ميزت تبعا لخواصها الفيزيائية والميكانيكية. النتائج المستحصلة دلت وبشكل واضح على الالتصاق الجيد بين مكونات المركب. كما ظهرت تغييرات في الكثافة ومقاومة الماء، قوة الانضغاط والصلادة.

Introduction

A composite is a material developed by combining two or more components, one of which is a structural component (glass fiber, carbon fiber, vegetable fibers etc.) and the other is a matrix component, to obtain specific characteristics and properties [1]. The interest in natural fiber-reinforced polymer composites is growing rapidly due to their high performance in terms of mechanical properties, significant processing advantages, excellent chemical resistance, low cost and low density. These advantages place natural fiber composites among the high performance composites having economic and environmental benefits.

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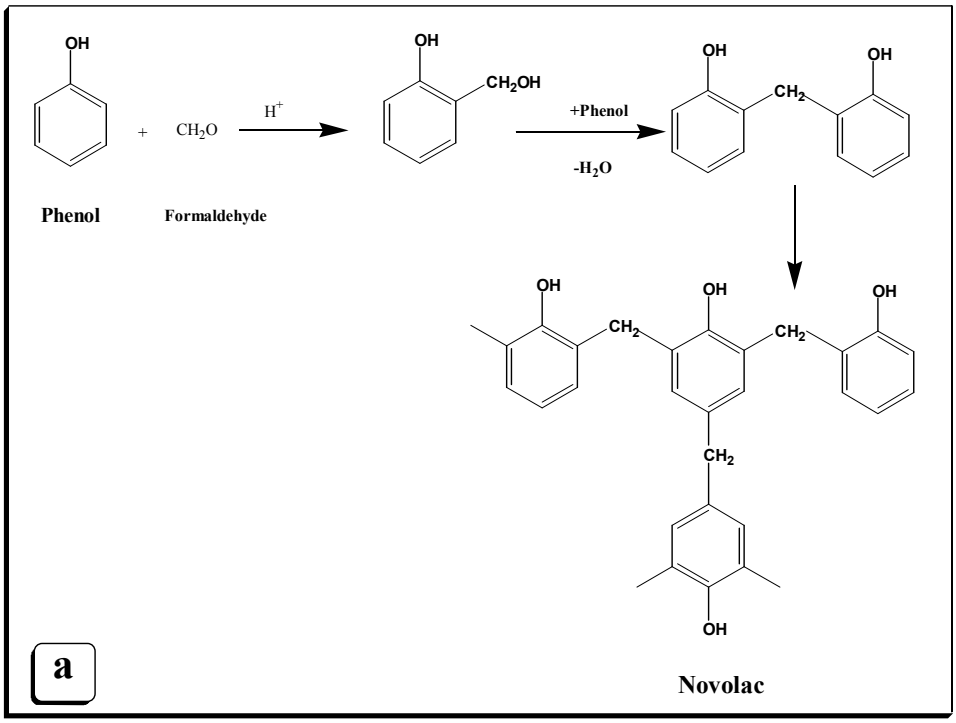
Natural fiber-reinforced thermoplastic composites form a new class of materials which seem to have good potential in the future as a substitute for wood-based material in many applications [2].

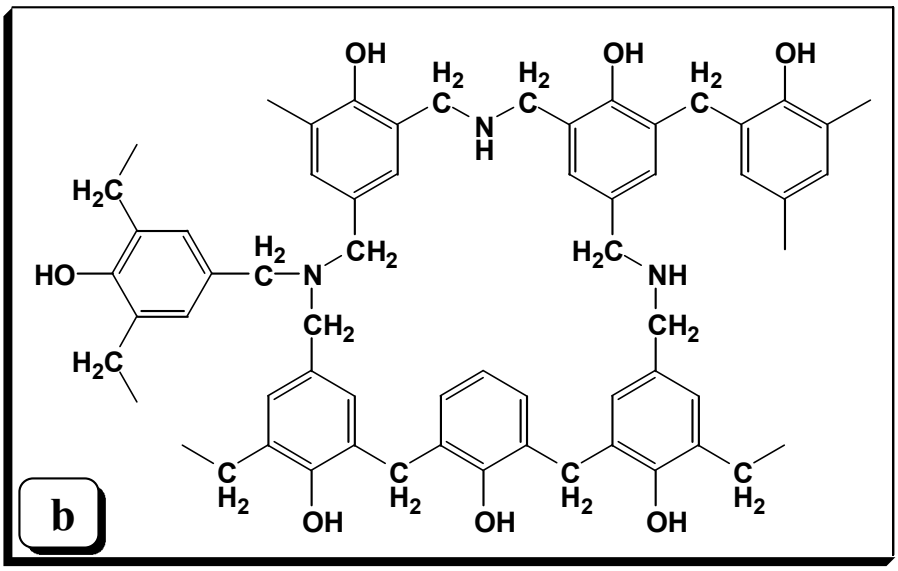
Recent years have witnessed rapid growth in the use of polymeric composites reinforced with fiber, producing a combination of high performance, great versatility, and other advantages at a favorable cost. One of the fibers used for these polymeric products, cellulose fiber, has become an important class of strengthening materials [3,4]. Agrawal et al. [5] reported that plant fiber properties directly influence the physical parameters of the fiber-reinforced composites. Fiber properties are controlled by the molecular fine structure of the fibers which is affected by growing conditions and the fiber processing technique used. Wood fibers possess moderately high specific strength and stiffness and can be used as reinforcement in polymeric resin matrix to make useful composite materials.

Phenolic resins are some of the principal thermo-fixed synthetic polymers, the third most important polymeric matrix for composites, and are also known for their high temperature resistance [6]. Pure phenolic resin can be obtained through the condensation reaction between phenol (C_6H_5OH) and formaldehyde (CH_2O), producing methylene bridges between the phenol molecules (Figure 1)[7,8].

In the presence of given reagents, like hexamethylene tetramine as an example, this resin can form crosslinks under the influence of light or heat, resulting in a rigid material. The material forms a three-dimensional network that will not soften on subsequent heating and can be removed from its mould without the need to wait for it to cool [8]. Due to the widespread use of phenolic resin, composites have diverse applications, such as laminates for table-top coverings, desks, dividers, doors, brake pads, moulded electrical components, etc. [1].



(Figure 1: a) Condensation reaction for the formation of novolak



(Figure 1: b) Fabrication of moulding

The present study aimes at developing and characterizing the physical and chemical properties of a new type of composite material, using phenolic resin as the polymeric matrix and *caria species* fiber as the strengthening element.

This study is developed in two phases:

a) development of the composite, involving molasses alkalinizeation, fiber drying, grinding and granulometric classification, formulation of the composite, and pressing and,

b) characterization of the properties of the composite.

Experimental Work

Materials:

1) Reagents for preparation of the novolak are:
   Phenol, 37% aqueous formaldehyde solution, 98% sulfuric acid (H_2SO_4) and water.
2) Reagents for fabrication of moulding are:
   Calcium oxide (CaO), calcium stearate, molasses, *caria species* fibers, and hexamethylene tetramine.

Equipments:

Three necked flask (250 ml), mechanical stirrer (Janke & Kunkel GmbH & Co. KG Ika-Weark Type RW18), reflux condenser, and sand bath.

Methods:

Test bodies of the composite were prepared with different grain sizes molasses and fiber compositions.

a) Preparation of Phenol Formaldehyde Resin

(1 mole) of phenol, and (4.44 mole) of (37%) aqueous formaldehyde solution were placed in a (250 ml) three necked round bottom flask connected to reflux condenser. The flask was warmed slightly on a sand bath to (100ºC) to melt the phenol then it was shaken to obtain a homogeneous solution. (0.5 ml) of concentrated sulfuric acid which was added to a (10 ml) of water in a little beaker, and then this

solution was poured into the flask. Then the exothermic reaction startsed quickly and mixture was kept at (100ºC). After (15 min) the reaction completed. Water was discarded and condensed solution (the resin) was taken to the next step [9].

b) Neutralization of the Molasses

The molasses used in this study results from extraction of the beat syrup by grinding. As a result of the bacterial flora present in the molasses, the fermentation reactions proceed rapidly, leading to the formation of volatile products with unpleasant odors, as well as acidifying the medium. Therefore, this degradative process was neutralized by calcium oxide (CaO). Excess of calcium oxide can be utilized to trap residual acid from condensation reaction (step a).

c) Dough Preparation

Fibers were dried in a drying and sterilization oven (LABSCO-memmert-12880-KI). After drying they were grinded in a mill and sieved into two sizes, (32-80 mesh) and (80-200 mesh). (5 g) from each size of fiber was added to the neutralized molasses and dried in the oven at (110ºC) for 3 hours. The dried dough then was ground in the mill. The granulometric separation of the dried dough was carried out in a granulometric sieve separator, in which the size ranges separated are indicated by the following code: G1 (32-80 mesh) and G2 (80-200 mesh).

d) Formulation of the Test Body

Phenolic resin (phenol formaldehyde) obtained from step (a) was used in this study. Hexamethylene tetramine (hexamine), which acts as a reticulation agent, was used in the formulation of this resin. Calcium stearate was used to improve the mobility of the product within the mould and the interaction between particles.

The test bodies varied in composition according to the quantity of resin and fiber and the grain size. In order to assess the composition and size range that represented the optimal properties of the system under study, a complete 2^2 experimental planning was used, in which a planning matrix was elaborated to minimize and to organize the experiments. In this planning the influence of the two factors, composition of the test body and grain size of the fiber for density, absorption of water, compression strength and hardness were assessed.

According to the experimental planning matrix, four experiments were performed for each assay; Table 1 summarizes the experiments carried out, in which the responses to each experiment were analyzed in graphs related to each assay type.

Table 1: Experiments conducted based on the experimental planning matrix.

EXP.	COMPOSITION OF SPECIMEN (%)		GRAIN SIZE OF DOUGH (MESH)
	Resin	Dough	
1	29	69	80-200
2	69	29	80-200
3	29	69	32-80
4	69	29	32-80

C1 : 69% resin, 29% dough, and 2% hexamine + stearate
C2 : 29% resin, 69% dough, and 2% hexamine + stearate
G1 : 32 – 80 mesh;
G2 : 80 – 200 mesh

e) Pressing

The phenolic resin, together with the dough and the additives, was mixed in a container, and the final mixture (physical mixture) was homogenized. After homogenization of the mixture, the pressing phase was carried out using a heated hydraulic press (NYETASERU England) to bring about the thermo-fixation of the phenolic resin. A pressure of $150kg_f/cm^2$ was employed for 10 to 15 min at a temperature of approximately 170º C.

Characterization of the Resin (Novolac)

a) Infrared Measurement

Infrared analysis was carried on the phenol-formaldehyde resin (novolac) using PYE-Unicam Ltd. and nunjol as solvent. The infrared spectrum of resin has an absorption whose peak is sharp and weak at 3650-3590 cm^{-1} whichys related to O-H stretch-free indicating the presence of phenols. The intensity of the absorption at region 2800-2700 cm^{-1} is medium and indicates C-H stretching vibration of –CHO (2 bands) confirming the presence of aldehydes [10].

b) Solubility

The resin solubility was identified and showed that resin is soluble in ethanol, acetone and paraffin liquid [11].

Characterization of the Composite

a) Density and Specific Gravity

The density of the test bodies prepared in this study was determined according to the ASTM D792-66 standard [12], by displacement of liquid and determination of the change in weight. Portions of a sample may differ in density because of difference in crystallinity, composition (types or portion of resin and fiber). Density was calculated by weighing the specimen in air to the nearest 0.1 mg and then the specimen weighted in water rapidly in order to minimize absorption of water by the specimen.

Specific gravity represents the ratio of the weight in air of a unit volume of the portion of material at 23°C to the difference between the weight in air and its weight in gas free distilled water of an equal volume

Sp.gr. $23/23^oC = a/(a - b)$

a: apparent weight in air. b: apparent weight in water.

While density is:

D^{23C} g/cm^3 = Sp.Gr. 23/23ºC × 0.9975

b) Water Absorption:

The test for rate of water absorption is a guide to the proportion of water absorbed by a material and there is a relationship between moisture and electrical or mechanical properties.

The water absorption assay was calculated according to the method described in the ASTM D570 – 77 [13]. The dried molded specimen in the form of disk 30 mm in

diameter and 3.2 mm in thickness was weighed to the nearest 0.001 g and then immersed in a container of distilled water maintained at a temperature of (23 ± 1ºC) for (24 + 1/2 h – 0 h) then removed from water and wiped off with dry cloth and weighted to the nearest 0.001g. The percentage increase in weight during immersion was calculated as follows:
increase in weight,was % = (wet wt. – dry wt.)/dry wt. ×100

c) Compression Strength

ASTM D695-77 describes the equipments and methods used to accomplish the compression strength as follows:

1. Measure diameters of specimens to the nearest 0.01 mm. then calculate and record the minimum value of the cross-sectional area.
2. Place the test specimen between the surfaces of the compression tool, taking care to align the center line of its long axis with the center line of the plunger and to ensure that the ends of the specimen are parallel to the surface of the compression tool.
3. Record the maximum load carried by the specimen during the test (usually this will be the load at the moment of rupture).
4. Calculate the compressive strength by dividing the maximum compressive by original minimum cross-sectional area of the specimen. Express The resultis explesscde in mega Pascal.

The compressive assays were carried out using (Compressive Strength Tester MARUI & Co. LTD Japan).

d) Hardness

The Rockwell hardness (HRR) was measured by (Dia Tester 2RC Karl Kolb D-6700) according to ASTM D 785-65(1976) [15], using R-scale with a 12.7 mm indenter and 60-kg major load. The test specimen was then placed in position on the anvil and minor load of 10 kg was applied to make the zero setting with 10s. The major load was applied immediately after the zero setting has been completed. The actual scale divisions representing indentation should be counted. A full revolution of the needle represents 100 divisions. The hardness determined by this procedure shall be known as the alpha, α, Rock-well hardness number and calculated as follows:
α Rock-well hardness number = 150 – total indentation under load.

Results and Discussion

A photograph of the test body of the composite obtained can be seen in Figure 2 below.

Figure 2: A photograph of the test body of the composite

Figure (3) exhibits the density values for the composites in different percentages of dough and grain size distributions. It can be seen that the density of the composites in relation to percentage of fibers suffered a reduction with the increase in the fraction of fibers. This is due to the low density of fiber (0.654 g/cm^3) in relation to the phenolic resin. The grain size, does not show significant influence on the density of the composite.

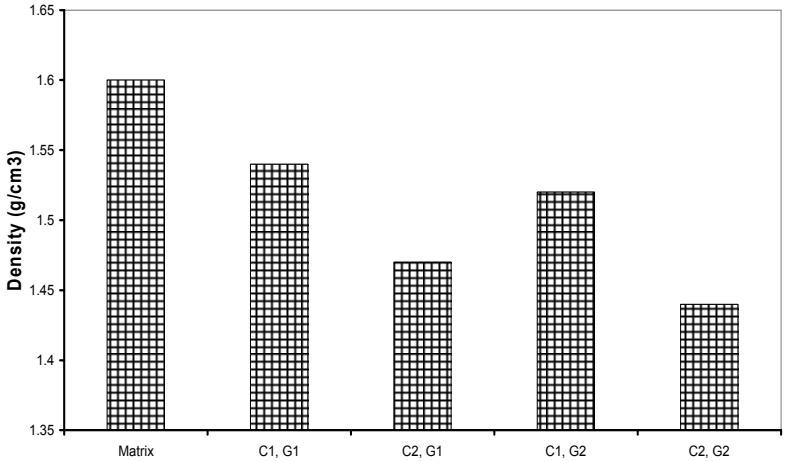


Figure 3: Density of composites as a function of percentage of fiber and grain size.

Water absorption in polymers is assessed by the absorption of humidity, resulting in an increase in the dimensions of the piece, which hinders their application in precision situations. In addition, the variation in humidity can result in the formation of a network of micro-fractures on the surface of the artefacts and alter their electrical and mechanical properties. The sensitivity to water is related to the grade of cure of phenolic resins; for example, in the case of incomplete cure, the laminates in contact with the water swell change their size and undergo delaminating, according to Mano[1]. Water absorption experiments showed that it is in the order of 0.4% for the matrix, whilst the composites with other percentages of fiber showed slightly higher water absorption percentage (max. 0.74%). Results are shown in Fig4. For hydrophilic fibers, such as cellulose fibers, there is an increase in water absorption. But the low values of water absorption obtained may be due to the strong adhesion

between the fiber and the matrix. This may be due to the existence of Tri-basic Saccharate of Calcium ($C_{12}H_{22}O_{11}.3CaO$), which is obtained from the reaction between the molasses and calcium oxide, known as Steffen process [16], resulting in a satisfactory interaction between the fiber and the matrix.

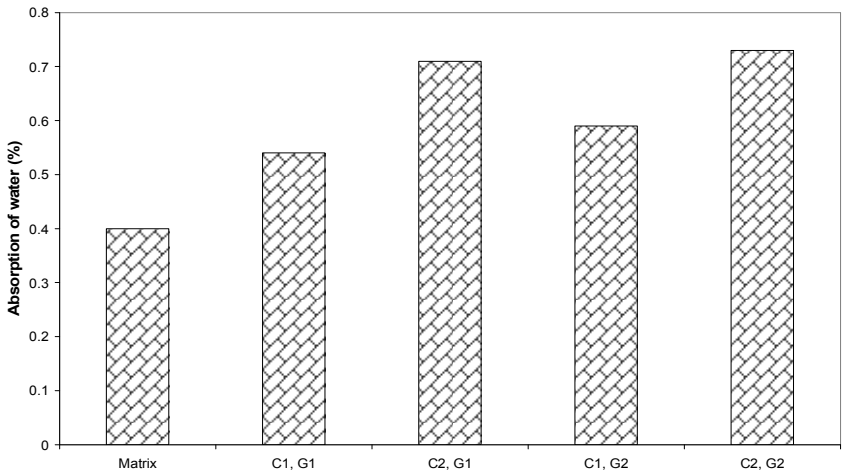


Figure 4: Absorption of water by the matrix and composites with different percentages of dough and grain size

Compressive strength of the body is the property that is highly dependent on the interfacial adhesion between the phases present, since if the adhesion is not perfect, there is a strong probability of creating a flaw that would lead to breakage of the material in the interfacial region. The absence of adhesion leaves this region weaker [17-19]. Fig (5) shows the compression strength values for composites in different dough percentages and grain sizes.

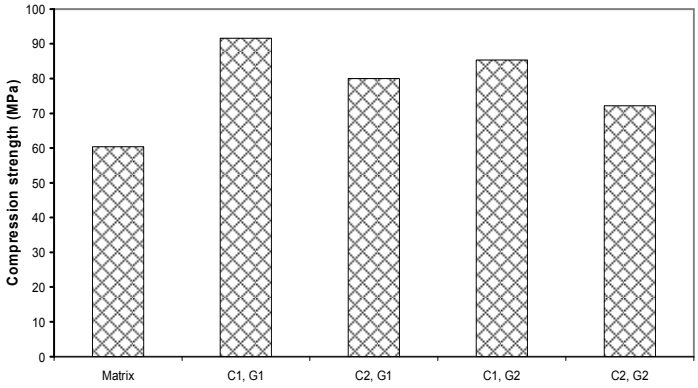


Figure 5: Compression strength for the matrix and the composites with different percentages of dough and grain sizes

It was found that the compression strength for 69% dough is greater than that for the fraction with 29%; these values are within the expected range, according to similar results obtained by Joseph et al [20], using short fibers of sisal in a polyester matrix with fiber fractions between 10% and 50%. The resistance to fracture of the composites increased with fiber fractions which is a function of dough fractions. The influence of fiber and dough granulometry on the compressive strength, in the case of

69% dough fractions, for grain sizes of 32 to 80 mesh, was 6.8% higher than for grain sizes of 80 to 200 mesh. This behavior was similar to 29% dough fractions with the variation of 9.78%. This effect was probably due to the size of the granulometric bands used, above the critical length. According to Joseph et al.[20], in composites reinforced with short fibers there is a critical length of fiber necessary if maximum resistance is to be achieved. If the length of the fiber employed as reinforcement is shorter than the critical length, the fiber will be loosened from the matrix and the composite will break at low tensions.

Fiber aspect ratio, i.e. the length to diameter ratio of a fiber, is a critical parameter in a composite. An expression relating critical fiber aspect ratio (l_c/d) to interfacial shear stress (t_y) has been proposed by the following equation [21]:

$$\mathbf{l_c / d = S_{fu} / 2\ t_y}$$

where:
l_c : critical fiber length
d : diameter
S_{fu} : fiber ultimate strength in tension
t_y: interfacial shear stress

Hardness measurements showed that the Rockwell hardness slightly increases as the polymer percentage increases and vice versa, also it is higher for fine fibers than it is for coarse fibers. Results are tabulated in Table 2. These results are within the expectation as the hardness of fiber is less than that of the resin.

Table 2: Rockwell hardness for different sample compositions and grain sizes

SAMPLE	ROCKWELL HARDNESS
Matrix	HRR 112
C1 G1	HRR 116
C2 G1	HRR 110
C1 G2	HRR 113
C2 G2	HRR 108

The factor that may have contributed to these results is the strong adhesion between the fiber and the matrix, increasing the rigidity of the material and the mechanical properties of the composite.

Conclusions

From the results presented in this study it can be seen that the use of *caria species* fibers as a strengthener in phenolic resin represents a very viable alternative.
The results obtained demonstrate the good adhesion between the fiber and the matrix. The density assays of the composites under study reveale a decrease of (10 %) in the densities of the test bodies with (29%) resin fractions, while the variation in density with the granulometry of the fibers not significant (in the range of 2%). The water

absorption assays show that the maximum increase in water absorption is in the range of (82.5%). Also, in this case the influence of granulometry was not significant.

The results obtained with the compression strength assays demonstrate that it increases with the proportion of fibers, reaching a maximum value at (29%) fibers, which is (51.7%) whilst at a proportion of (69%) fibers there is a decrease in these values to (32.5%), due to the excessive interaction between the fibers, decreasing the values for compression strength of the composite. Hardness results show that it is slightly aeffected by the addition of fibers.

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