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Thème

**Synthesis and Characterisation Of Poly Phenolic Composite Used
In Electrical Industry**

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Dedication

El Khalwa Ennabawia El Mohammadia

MOM

DAD

Shaikhi: Ahmed Yehia MORSLI

My brothers

My family

My teachers

My freinds

المخلص

يتناول هذا العمل صناعة مادة الريزول^١ أو ما يعرف ب: الريزول الفينولي الذي يعد من عائلة البوليميرات و الذي يمتاز بخاصية العزل الكهربائي و أغلب إستعمالاته في هذا المجال لا سيما تلك المتعلقة بالتوترات المرتفعة, و هنا قمنا بصناعته و تحديد خواصه و قدراته فمنها الكيميائية: كغمره في مذيب الطوليان, و خواصه الكهربائية بتمرير تيار عالي خلاله بواسطة أسلاك مثبتة خلاله بأبعاد منتظمة لقياس الناقلية و المقاومة, و خواصه الميكانيكية بإجراء تجربة شاربي لقياس الصلابة و التماسك.

الكلمات المفتاحية: الريزول – البوليميرات – التوترات المرتفعة – مذيب الطوليان – تجربة شاربي.

Résumé

Ce travail porte sur la fabrication du matière de Risol, connu sous le nom de: résine phénolique, qui est classé au famille des pollimères, qui se caractérise par la caractéristique de l'isolation électrique et la plupart de ses utilisations dans ce domaine, en particulier celles liées aux haute tension, et nous avons le fabriqué et déterminé ses propriétés et caractéristiques, Comme il est immergé dans le solvant tolluene et ses propriétés électriques en faisant passer un courant élevé à travers des fils fixés à lui de dimensions régulières pour mesurer la conductevite et la résistance, et ses propriétés mécaniques en effectuant une expérience de Sharpy pour mesurer la dureti et la cohésion.

Mots-clés: Resol - Polymères – Haute Tension – solvant de tolluene – Expérience de Charpy.

Abstract

This work deals with the manufacture of the risol material, which is known as: phenolic resin, which is a family of polymers, which is characterized by the characteristic of electrical insulation and most of its uses in this area, especially those related to high tensions, and here we have manufactured and determine its properties and capabilities, As it is immersed in solenoid solvent, and its electrical properties by passing high current through wires fixed in it to regular dimensions to measure the conductivity and resistance, and its mechanical properties by conducting a Sharpe experiment to measure rigidity and cohesion.

Keywords: Risol - Polymers - High Tensions - toluene solvent - Charpy experiment

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Abreviation

PF: Phenol Formaldehyde

HMTA: HexaMethylene TetrAmine

PH: Hydrogene potential

ASTM: American Societe Test and Mesure

CFRC: Carbon Fiber Reinforced Carbon

DC: Direct Current

CVI: Chemical Vapor Infiltration

PVAC: PolyVinyl Acetate

3D: Three dimentionel

Bcc: Body-centered cubic

DBTT: Ductile-brittle transition temperature

PCB: polychlorobiphényles

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Overview

Phenol-formaldehyde resin (PF), also known as phenolic resin, any of a number of synthetic resins made by reacting phenol (an aromatic alcohol derived from benzene) with formaldehyde (a reactive gas derived from methane). Phenol-formaldehyde resins were the first completely synthetic polymers to be commercialized. In the first decades of the 20th century, Bakelite a trademarked phenolic plastic, revolutionized the market for molded and laminated parts for use in electrical equipment. Phenolics are still very important industrial polymers, though their most common use today is in adhesives for the bonding of plywood and other structural wood products. The chemical composition of phenol and formaldehyde and their combination into networks of permanently interlinked large molecules are widely reported in the literature.

In industrial practice, there are two basic methods for making the polymer into useful resins. In one method, an excess of formaldehyde is reacted with phenol in the presence of a base catalyst in water solution to yield a low-molecular-weight prepolymer called a resole. The resole, frequently in liquid form or solution, can be cured to a solid thermosetting network polymer by, for instance, sandwiching it between layers of wood veneer and then heating the assembly under pressure to form a plywood.

The other way involves reacting formaldehyde with an excess of phenol, using an acid catalyst. This process produces a solid prepolymer called a novolac (or novolak), which resembles the final polymer except that it is of much lower molecular weight and is still thermoplastic (that is, it can be softened by reheating without undergoing chemical decomposition). Curing can be accomplished by grinding the novolac to a powder, mixing it with fillers such as wood flour, minerals, or glass fibres, and then heating the mixture in a pressurized mold. In order to be cured to a thermosetting resin, novolacs require the addition of more formaldehyde or, more commonly, of compounds that decompose into formaldehyde up on heating. [1]

History

A thermosetting amino resin that is made by reacting phenol with formaldehyde. Discovered in 1907 by Leo Baekeland and sold as Bakelite in 1909, phenol formaldehyde resin was the first true synthetic plastics. Phenolic resins can be made with either excess formaldehyde (resol) or with an excess of phenol (novolac). Resols are soluble in alcohol while novolacs are solid at room temperature. Both require crosslinking to form a hard plastic that is brittle but has good resistance to water and biodegradation. In the early 20th century, phenol formaldehyde resins were used for dark color molded plastic products sometimes filled with cellulose, wood flour, or mineral powders. Resol phenolics are currently used for plywood, textile sizing, leather processing, paper strengthening, foams and chemical resistant coatings. Novolacs are used for fibers, adhesives, molded parts, circuit boards, and mechanical fittings.

Although they are now approaching their centenary, phenolic resins continue to be used for a wide variety of applications, such as moulding powders, laminating resins, adhesives, binders, surface coatings and impregnants. Until very recently the market has continued to grow but not at the same rate as for plastics materials in general. For example, in 1957 production of phenolic resins was of the same order as for PVC and for polyethylene and about twice that of polystyrenes. Today it is less than a tenth that of polyethylene and about one-third that of polystyrene. In the early 1990s it was estimated that production in the USA was about 120 000 t.p.a., in Western Europe 580 000 t.p.a. and in Japan 380 000 t.p.a. With most markets for phenolic resins being long-established but at the same time increased competition from high-performance thermoplastics the overall situation had not greatly changed by the end of the 1990s.

Phenolic moulding powders, which before World War II dominated the plastics moulding materials market, only consumed about 10% of the total phenolic resin production by the early 1990s.

In recent years there have been comparatively few developments in phenolic

resin technology apart from the so-called Friedel-Crafts polymers introduced in the 1960s and the polybenzoxazines announced in 1998 which are discussed briefly at the end of the chapter.

Phenolic resins are also widely known as phenol-formaldehyde resins, PF Resins and phenoplasts. The trade name Bakelite has in the past been widely and erroneously used as a common noun and indeed is noted as such in many English dictionaries. [2]

Chapter I

Bibliographic synthesis

Phenolic Resins

I.1) Introduction

Phenolic resin or phenol formaldehyde (PF) resin is considered to be the first polymer material produced commercially from a low molecular weight compound. In other words, phenolic resins were the first truly synthetic resins to be exploited commercially. The concept of producing high molecular weight substances from oligomeric resins (phenolic resin) with or without filler was first discovered by Leo H. Baekeland. This pioneering concept has been subjected to continued technological development and perfection over the years, and has reached the sophisticated thermoset resin composite technology available today.

Phenolic resins are prepared by a step-growth polymerisation of formaldehyde and phenol or phenol derivative using an acid or a base catalyst. The product type and the quality largely depend on the ratio of the reactants used and the nature of the catalyst. Phenolic resins are available in two varieties:

- 1) novolac, which is a thermoplastic type and can be used as it is or can be cured with hexamethylene tetramine (HMTA) to get a crosslinked structure. This can also be viewed as a reactive intermediate, and can be transformed into other groups so different types of structures can be generated;
- 2) resole, which is a multifunctional reactive compound and can be cured thermally without a catalyst or an acid catalyst. [3]

I.2) Properties and uses of Phenolic Resins

In Phenol formaldehyde wide range of molding powders is available in which the composition of the resin, fillers etc is varied to provide mouldings suitable for many purposes. Here compression and transfer processes commonly used. The phenolic resin's polarisability is 10^{-24}cm^3 and Enthalpy of vaporization is 43.52 kJ/mol. It's polar surface area is 9.23 \AA^2 . It has 1 H bond donor and 1 H bond acceptor. 72.5 °C is it's flash point, 181.8 °C at 760 mmHg it's boiling point and 0.614 mmHg at 25°C is it's vapor pressure. Phenolic resin has the colour is Resin itself tends to be amber-colored. It has Wide variation depending on fillers and nature of resin. It is Smooth and has lustrous surface. Usually it

seems hard and rigid, with good dimensional stability. It may be brittle in thin sections with low impact strength.

It is very easy to mould. Phenolic resin has Retain properties at freezing temperatures. The phenol formaldehyde have Improved strength and dimensional stability and Improved impact resistance and also cast resins. It's color is good normally transparent and may be colorless It is good dimensional stability on heating up to about 300 degree F Poor conductors of heat , so that handles of pans etc stay cool to touch. It can burn only with difficulty. Age of phenolic resin is negligible deterioration. Electrical if we will verify then it is good electrical insulators, Laminated Plastics. Properties generally related to those of moulded plastics. [4]

I.3) Uses or Application

Phenol formaldehyde have so many uses in different industry. Phenolic resins are mainly used in the circuit board production that is for making circuit board like PCB ...etc this phenolic resins are used. In Electrical equipment also it is needed ,caps, handles, buttons, radio cabinets, furniture, knobs, vacuum cleaner, cameras, ash trays, engine ignition equipment.It is also used in Laminated Material like laminated sheets, rods and tubes are made in great variety from fabric, paper, wood veneers etc impregnated with phenolic, resins providing a range of materials of widely differing properties. [5]

I.4) Type of Phenolic Resins

Novolac

Novolac is produced by the reaction of formaldehyde with an excess amount of a phenol or a phenol derivative in the presence of an acid catalyst. The ratio of phenol to formaldehyde used is in the range 1.49 to 1.72. The reaction in acid medium involves initial protonation of hydrated formaldehyde followed by electrophilic substitutions in the *ortho* and *para* position (electron-rich position unlike the *meta* position). At low temperature, only addition of formaldehyde to phenol occurs and *o*- or *p*-methylol phenols are formed. At higher temperature,

the condensation reactions of methylol phenol with phenol and/or methylol phenol occur, leading to the formation of a prepolymer and the desired resin [1, 2]. Water is formed as a byproduct. The reaction scheme is shown in **Figure.1**. The condensation of methylol phenol can generate three types of methylene bridges: *o,o'* (condensation of two *o*-methylol phenols), *o, p* (condensation of an *o*-methylol phenol with a *p*-methylol phenol) and *p, p'* (condensation of a *p*-methylol phenol with a *p*-methylol phenol). The reaction in the presence of a strong acid such as sulfuric acid or phosphoric acid produces the distribution methylene linkages (*o,o':o,p:p,p'*) close to the statistical value 1:2:1. However, a weak acid catalyst like oxalic acid leads to the formation of more *p,p'* linkages. A typical distribution of methylene linkages obtained for the synthesis of novolacs using sulfuric acid and oxalic acid are 25.9:48.5:25.9 and 23.3:49.1:27.6, respectively. [6]

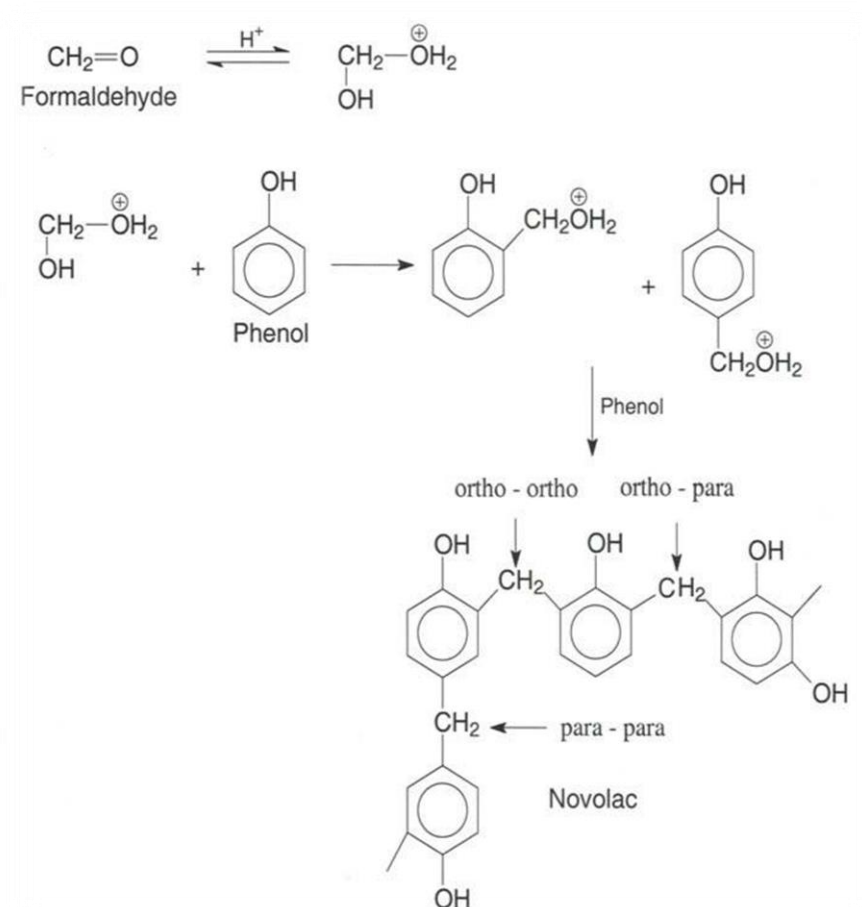


Figure.1 Reaction mechanism for the synthesis of novolac-type phenolic resin[3]

Resol

The Resol is produced by reacting a phenol with an excess of aldehyde under basic conditions.

In this case the formation of phenol-alcohols is rapid but their subsequent condensation is slow. Thus there is a tendency for polyalcohols, as well as monoalcohols, to be formed. The resulting polynuclear polyalcohols are of low molecular weight. Liquid resols have an average of less than two benzene rings per molecule, while a solid resol may have only three to four. a typical resol would have the structure shown in **Figure 2**.

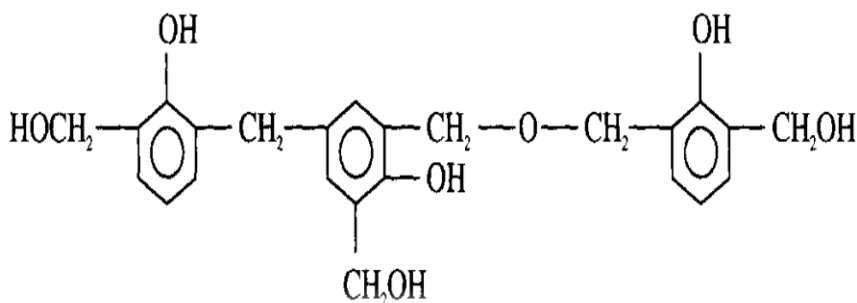


Figure 2: Reaction mechanism for synthesis resol[3]

Heating of these resins will result in cross-linking via the uncondensed methylol groups or by more complex mechanisms. The resols are sometimes referred to as one-stage resins since cross-linked products may be made from the initial reaction mixture solely by adjusting the PH. On the other hand the Novolaks are sometimes referred to as two-stage resins as here it is necessary to add some agent which will enable additional methylene bridges to be formed. [7]

I.5) Synthesis of Resole

Resole is produced by reaction of a phenol or a phenol derivative with an excess amount of Formaldehyde in the presence of a base catalyst. The reaction in basic medium proceeds through the addition of formaldehyde with the phenoxide ion, leading to the formation of *o*- or *p*-monomethylol phenol (along with some di- or

trimethylol phenol) as established by complexation via cyclodextrin or crown ether [2].

The reaction scheme for the synthesis of resole is shown in **Figure 3**.

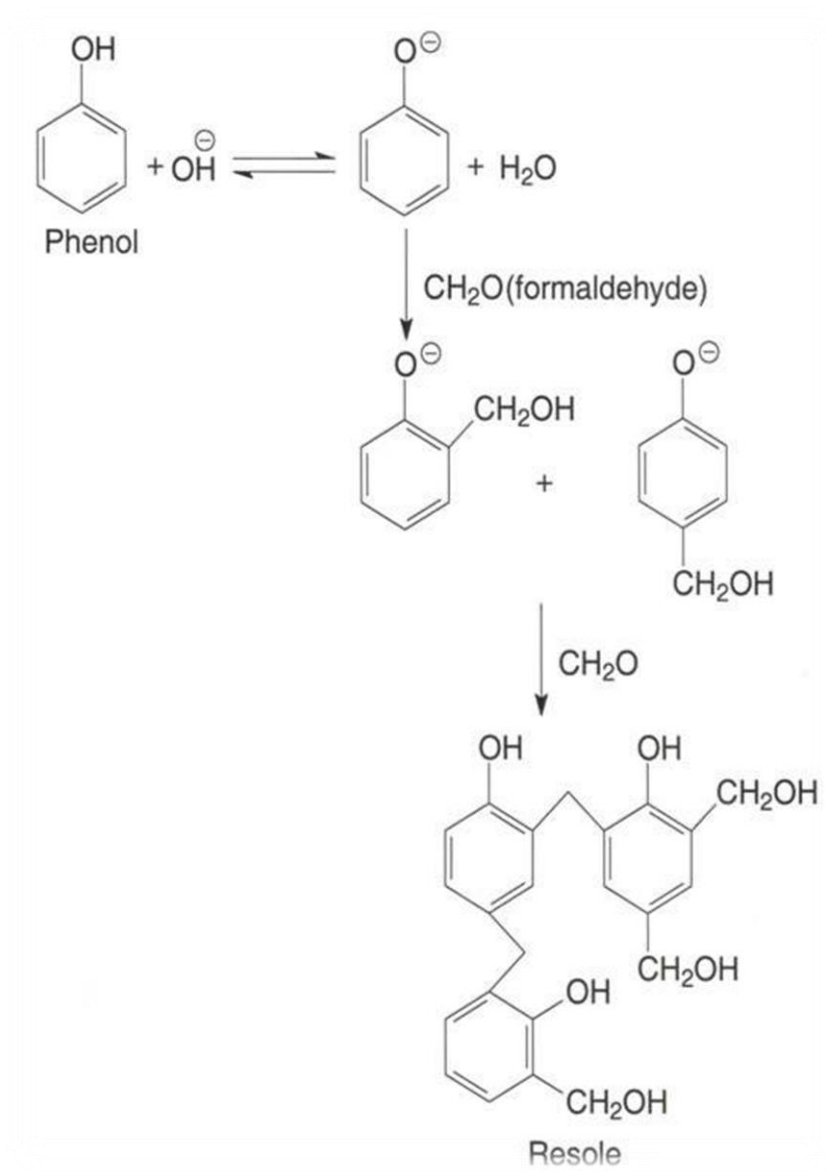


Figure 3: Scheme Reaction for the formation of resole-type phenolic resin[3]

I.6) Difference between Novolac and Resol

Novolac and resole are the products of phenol and formaldehyde, and are known as ‘phenolic resin’. The differences between novolac and resole are as follows:

Novolac is produced using excess phenol and an acid or metal salt catalyst, whereas resole is produced using excess formaldehyde and a basic catalyst.

Novolacs are mostly supplied in the solid form, whereas resoles are mostly supplied as a solution (using water or alcohol as a solvent).

Novolac is not self-curing; it requires an extra curing agent, whereas resole is self-curable without an additional catalyst.

Novolac has a long shelf-life, whereas resole has a limited shelf life (<1 year).

Novolac can be used as a thermoplastic and can be readily modified by reacting with the terminal hydroxyl groups. Modification of resole is comparatively difficult due to a gelling problem. [8]

Table 1: Characteristics of the Resins [9]

Type	Resol			Novolac		
Expremet	1	2	3	1	2	3
F/P molar ratio	1.3	1.9	2.5	0.5	0.7	0.9
M_n	240	380	400	380	390	390
M_w	460	630	670	540	560	580
M_n/M_w	1.92	1.66	1.67	1.44	1.42	1.49
Nonvolatile content (%)	59.2	53.5	50.4	46.6	45.4	45.9
Viscosity (mPa s)	157	445	1390	22.6	25.7	29.8

M_n : number-average molecular weight;
weight.

M_w : weight-average molecular weight.

I.7) Thermoset Resins

Thermosetting resins are characterised by a crosslinking reaction, which leads to the formation of a three-dimensional (3D) network structure. The basics of network structure and various evaluation methods for thermosetting resins were discussed in Chapter 1. The greatest advantage of thermoset resins is that they are processed from a low molecular weight compound (resin) unlike the high molecular weight macromolecules in the case of thermoplastics. This is why thermoset-based products can be moulded, in general, at a much lower temperature and pressure compared with thermoplastics. Another distinct characteristic of thermosetting resins is that their properties are not only dependent on the chemistry and molecular weight of the resin (as in the case of thermoplastics) but are also largely dependent on the crosslink density of the resin network. A wide range of properties can be achieved by simply adjusting the crosslink density of a network without changing the chemical structure. [7]

II) Characteristics and properties of Resol phenolic

I.8) Mechanical Properties

In virtually all applications, phenolic materials have to be subjected to a loading force in some way or other. Hence, the assessment of mechanical properties is very important for the design of phenolic materials for various applications. phenolic materials are more sensitive to the service temperature and other environmental effects compared with conventional materials. Hence, the data for mechanical properties, measured using conditions similar to a service environment, should be used for design rather than standard data available in the literature. [8]

We have some tests are presented in Table 2

Table 2: Mechanical properties of phenolic moulding compounds [9]

Moulding Compound	Tensile Strength (MPa)	Tensile Modulus (GPa)	Strain at break (%)	Flexural strength (MPa)	Compressive Strength (MPa)
RX-630	82.7	13.8	0.6	193	275.8
RX-660	55.2	11.7	0.5	137.9	227.5
RX-865	68.9	17.2	0.4	186	241.3

XB-22	75.8	7.6	1.0	151.7	234.4
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I.9) Adhesives properties

Wood bonding applications such as particleboard or wafer-board have traditionally used phenolic resin binders. Due to their specific "affinity" for wood and wood fibers, special liquid phenolic resins may be required for the specialty wood adhesives industry typically in combination with a polyvinylacetate (PVAc) backbone polymer. Plenco liquid phenolic resol resins with low free phenol and low free formaldehyde contents are available especially for use in adhesive applications. Plastics Engineering Company can also supply low ash content, soluble solid resol resins, and of course a wide range of novolac resin-hexa systems. [9]

I.10) Electrical properties

Nowadays, advanced composites plays an important role in the aerospace industry. Aircraft brakes and rocket nozzle throats belongs to the class of carbon fiber reinforced carbon (CFRC) which are components where the requirement to withstand high temperatures and thermal shock resistance is required. CFRC composites are materials based on carbon fibers embedded by a carbon matrix. The refractory characteristic of CFRC composites makes them able to retain mechanical properties under high temperature environments. Processing of CFRC composites are layed on two main routes, named liquid route and gas phase route, which requires heat treatment cycles. In the liquid processing route, which uses pitch (thermoplastic) or thermoset resin, high temperature heat treatment gives rise to solid carbon composite by converting the organic matrix to a carbon matrix. In the gas phase processing route, the decomposition from gaseous hydrocarbon (e.g., methane, propylene) result in carbons deposited on porous fibrous substrates. In this case, carbon gas bearing flux, temperature and pressure are tightly controlled and the process is called chemical vapor

infiltration (CVI). Processing routes of CRFC composites have been described in the literature.

Depending on application and design requirements thermoset resins based on phenol-formaldehyde are the most used. Also, easy processing and reasonably carbon yield makes phenol-formaldehyde polymers attractive for using as precursor matrix for CFRC composites. Conversion of phenolic resin/carbon fiber composites into CFRC composites is accomplished by rupture of the original molecular structure converting the polymer matrix to an amorphous carbon material by the action of heat.

During heat treatment important microstructural changes occur in the phenolic resin/carbon fiber composite which affect its thermomechanical behaviour. The main microstructural change is related to the conversion of the polymer matrix (insulator) into a conductive carbon material, resulting from molecular rearrangement, release of evolved volatiles and pore and crack formation. This also have an effect on physical properties, such as density, stiffness, strength, thermal conductivity, thermal expansion and electrical resistivity/conductivity. Therefore a number of experimental methods and techniques can be used for monitoring and measuring the progress of the heat treatment processes related to the conversion of a pristine phenolic resin/carbon fiber composite into a CFRC composite. For instance, weight changes during heat treatment of carbon materials can be monitored by thermogravimetric techniques, and dimensional changes can be monitored by dilatometric techniques.

Electrical resistivity has long been used as technique for monitoring and quality control of several important industrial process, such as graphite manufacturing and SiC manufacturing. So, changes in electrical resistivity (or electrical conduction) during processing can be associated to changes in materials microstructure, resulting in useful information for process understanding and as a quality control tool. For instance, monitored the processing of CFRC composites by CVI technique using electrical resistivity technique. Carbon fiber preform in the form of a needled punched felt with an apparent density of 0.18 g/cm^3 was used. The carbon fiber preform was fitted to a furnace, and an electric current, low voltage, passed through the preform producing heat energy by Joule effect. As a result the pyrocarbon was deposited

from natural gas (~98% CH₄), up to reaction temperature. The carbonization temperature was set at 900-1200 °C. Electrical resistance varied from 0.10 to 0.44 Ω after 67 hours of deposition and a final density of 1.78 g/cm³ was obtained.

Electrical resistivity (or electrical conductivity) of a solid material is a function of electronic charge multiplied by the electron movement e by the electron flux concentration, in the conductor. Specifically, the direct current (DC) technique is based on the application of an electrical potential V [volts, J/C] through the body of a material, where a current of magnitude i [amperes, C/s] flows through it. In many materials at low voltage values the current is proportional to voltage (V) and the electrical resistance (R) in ohms, which is described by the Ohm's law ($i = V/R$). The electrical resistance (R) unlike electrical resistivity (ρ) depends on the size and shape of the sample. The relationship between the electrical resistivity (ρ) and the electrical resistance (R) is given by Equation 1.

$$l R A \rho \Rightarrow \text{(Equation 1)}$$

Where l is length and A is cross-sectional area of material.

Among the physical properties, the electrical resistivity can change significantly with temperature. According to Arrhenius law as far as the temperature increases the electrical resistivity decreases.

Various experimental assemblies have been described in the literature for resistivity measurements. However, most of them refers to those employed at low temperature. Those employed at high temperature are designed to meet the specific requirements of high thermo-mechanical applications.

In this work, electrical resistivity was monitored during the progress of heat treatment of a 2D carbon fiber/phenolic resin composite towards conversion to a CFRC composite up to 1000°C. Electrical resistivity measurements were carried out in the direction of fibers axis. The measurements of electrical resistivity were conducted in accordance with the ASTM C611–98 standard. [10]

I.11) Chemical properties

Phenolic resins accommodate the harsh exposure of severe chemical environments. The inherent nature of phenolic resin provides an impervious shield to protect a variety of substrates from the corrosive effects of chemicals. Laboratory tests confirm minimal degradation from many chemicals after prolonged exposure, often at elevated temperatures. Typical exposures include gasoline, alcohol, oil, glycol, brake fluid, various hydrocarbons, and also weak acids and bases. Protective linings inside tankers used for bulk transfer of acids and other corrosive chemical products are often composed of phenolic resins. [11]

I.12) P.F composites

Phenol (C₆H₆O)

At one time the requirement for phenol (melting point 41°C), could be met by distillation of coal tar and subsequent treatment of the middle oil with caustic soda to extract the phenols. Such tar acid distillation products, sometimes containing up to 20% a-cresol, are still used in resin manufacture but the bulk of phenol available today is obtained synthetically from benzene or other chemicals by such processes as the sulphonation process, the Raschig process and the cumene process. Synthetic phenol is a purer product and thus has the advantage of giving rise to less variability in the condensation reactions.

In the sulphonation process vaporised benzene is forced through a mist of sulphuric acid at 100-120°C and the benzene sulphonic acid formed is neutralised with soda ash to produce benzene sodium sulphonate. This is fused with a 25-30% excess of caustic soda at 300-400°C. The sodium phenate obtained is treated with sulphuric acid and the phenol produced is distilled with steam (Figure 4). [12]

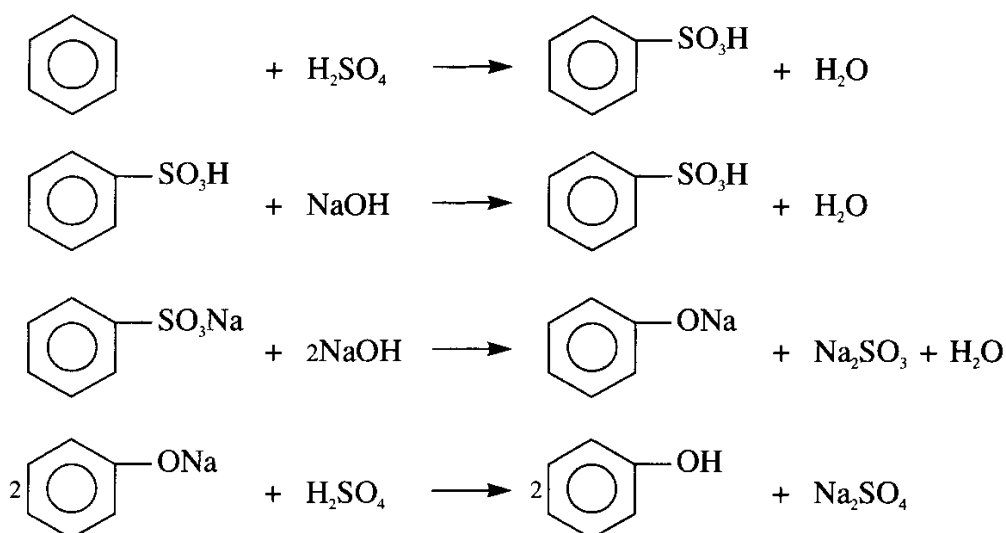


Figure 4: Scheme presented fabrication of phenol [10]

Formaldehyde (CH_2O)

Formaldehyde (methanal) is by far the most commonly employed aldehyde in the manufacture of phenolic resins.

It is normally used as an aqueous solution, known as formalin, containing about 37% by weight of formaldehyde. From 0.5-10% of methanol may be present to stabilise the solution and retard the formation of polymers. When the formalin is used soon after manufacture, only low methanol contents are employed since the formalin has a higher reactivity. Where a greater storage life is required the formalin employed has a higher methanol content, but the resulting increasing stability is at the expense of reduced reactivity.

Furfural is occasionally used to produce resins with good flow properties for use in moulding powders. [3]

Wood

Wood is a porous and fibrous structural tissue found in the stems and roots of trees and other woody plants. It is an organic material, a natural composite of cellulose fibers that are strong in tension and embedded in a matrix of lignin that resists compression. Wood is sometimes defined as only the secondary xylem in

the stems of trees or it is defined more broadly to include the same type of tissue elsewhere such as in the roots of trees or shrubs. In a living tree it performs a support function, enabling woody plants to grow large or to stand up by themselves. It also conveys water and nutrients between the leaves, other growing tissues, and the roots. Wood may also refer to other plant materials with comparable properties, and to material engineered from wood, or wood chips or fiber. Wood has been used for thousands of years for fuel, as a construction material, for making tools and weapons, furniture and paper. More recently it emerged as a feedstock for the production of purified cellulose and its derivatives, such as cellophane and cellulose acetate. As of 2005, the growing stock of forests worldwide was about 434 billion cubic meters, 47% of which was commercial.

As an abundant, carbon-neutral renewable resource, woody materials have been of intense interest as a source of renewable energy. In 1991 approximately 3.5 billion cubic meters of wood were harvested. Dominant uses were for furniture and building construction. [13]

Chapter II: Materiels and methods

Matériels and méthodes

II.1) chemicals products

In this current work, the chemicals synthesis of resol resins and composite nessesite the use of many chemicals.

The formulation uses a PHENOL solid crystals "100%" produced by: VWR CHEMICALS.

This crystals have a molar weight of: 94,11g/mol.

Additionally the Formaldehyde was produced by: BIOCHEM CHEMOPHARMA. This chemical was delivred in the form of a dilluated solution (37% - 41%) having a molar weight of: 30,02g/mol.

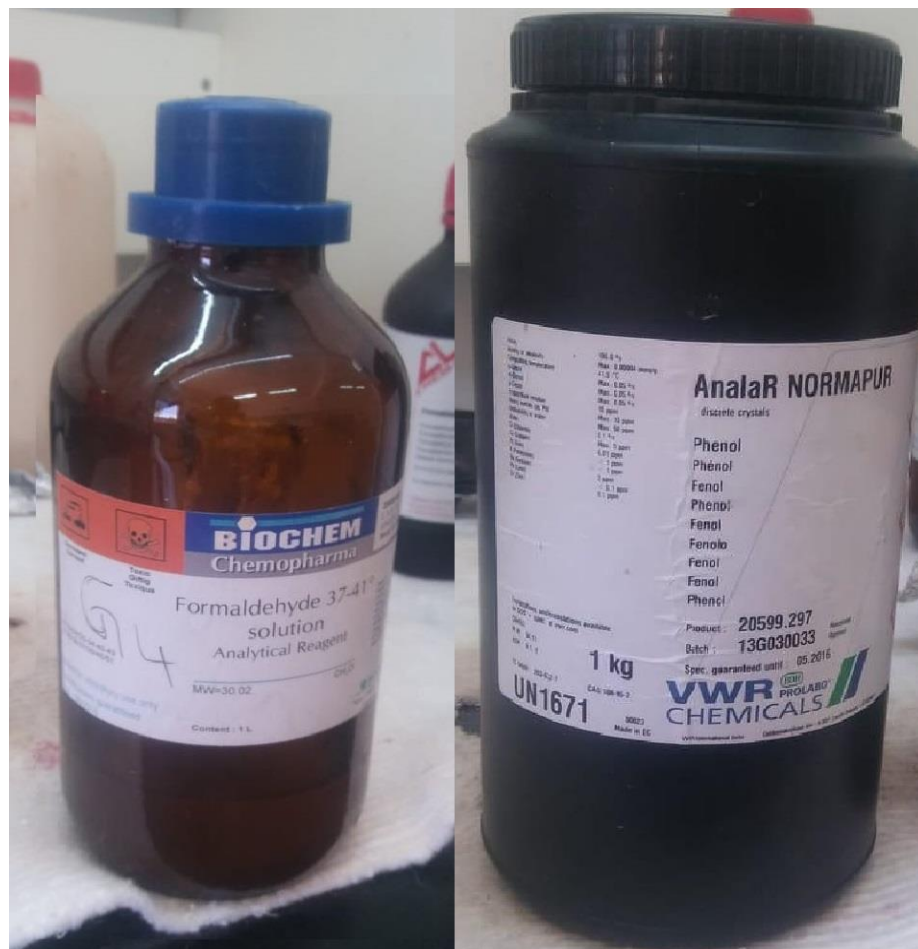


Figure 5: Phenol and formaldehyde solution.

The catalyst used in this reaction was: Sodium Hydroxyd "NaOH" produced by: SIGMA – ALDRICH as granuls (98%) it was diluted to a concentration of "0,47 mol" using distilled water prepared at a laboratory"GP" by a machine GFL.

The floor used in this study was collected from the sieve: $\text{Ø} < 80\mu\text{m}$.

To prepare the composite samples, Sawdust collected from cutting Red wood remains (floor). The Sawdust was then sieved using (BERA test Sieve) machine, using maximal vibration, the floor was placed at the higher sieve "1,25mm" after set ON, the machine kept sieve for a period of: 100min.

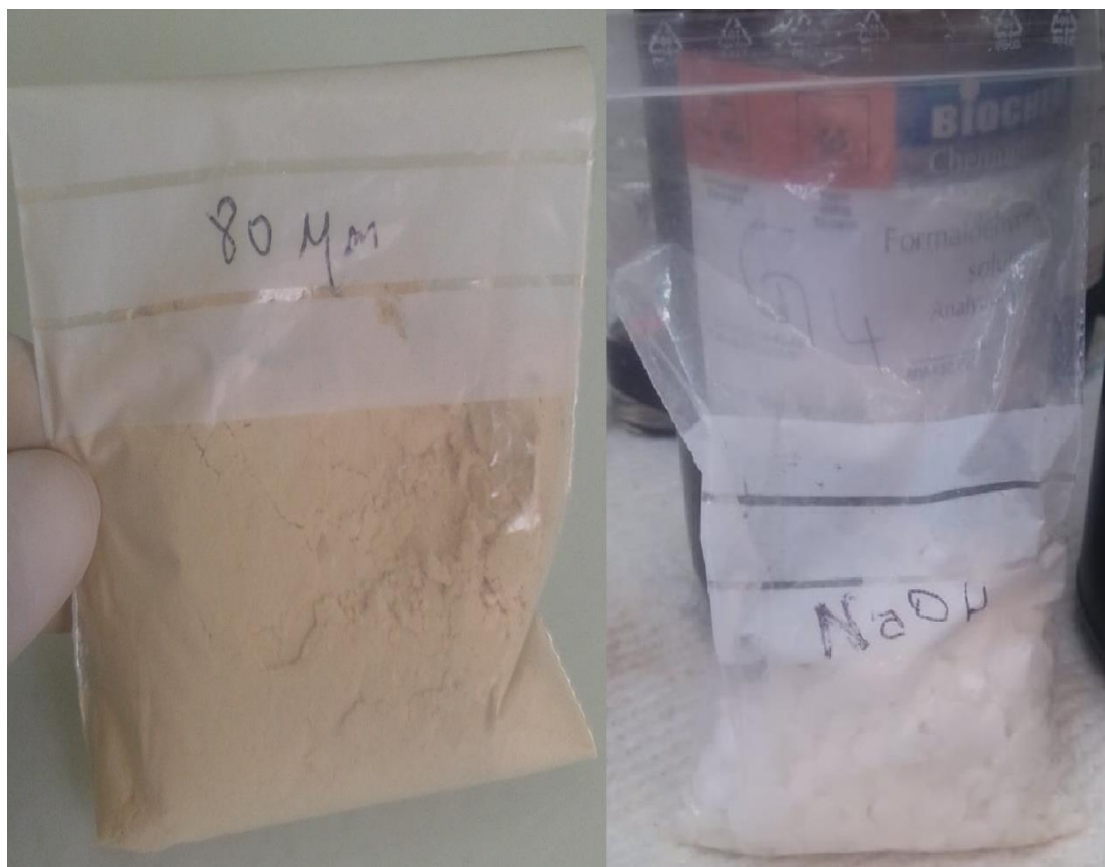


Figure 6: The chemicals additionally using in this study (NaOH and sawdust).

II.2) Resol synthesis

In order to produce the resol Phenol-Formaldehyd (PF) in GHARDAIA university laboratory did the following :

First, we weighed 27g of Phenol in a precised balance. On the other hand,we put some Sawdust wood particles of 80 μm radius, then we kept it into moisture absorber (Etuve) for one night. We added 3g of that sawdust to the phenol so that we gat a total weight of 30g. Next, we gathered that mixture together with 12g of 47% Naoh solution, 54g of formaldehyd and 12ml of distilled water in 500ml beaker from PYREX, and marked down the total weight $m=109,34\text{g}$. We put a beaker into a rond botom flask from ISOLAB connected to an intensive closed from the tap (as described in the protocol) under 50°C heat and speed rotation degree 2; for 90 min until changes its color from transparent to yellow, we raised the Temperature again to 90°C for One hour until it becam Red.

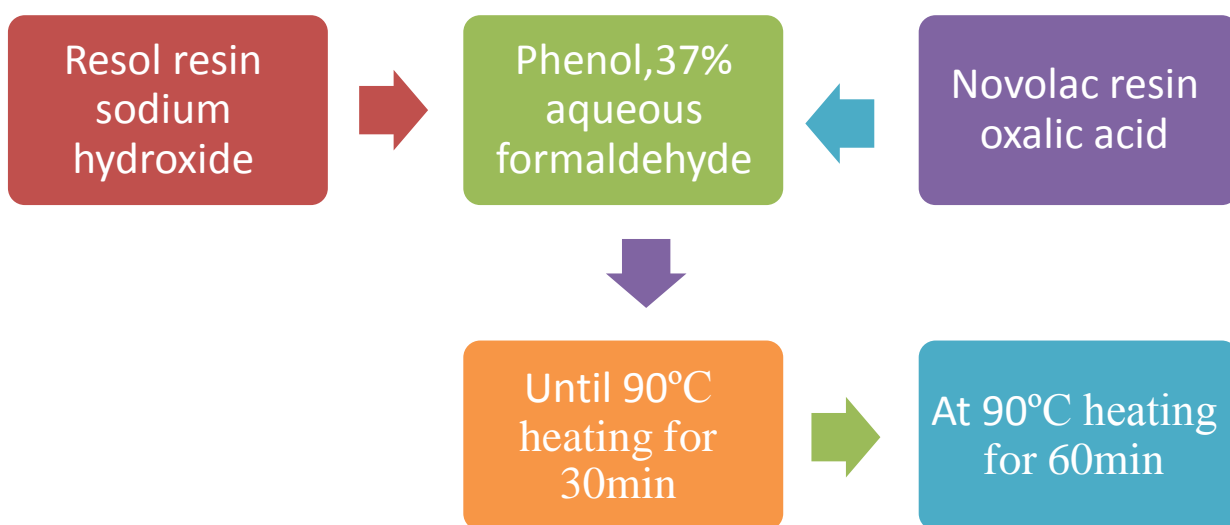


Figure 7:Scheme used in the preparation of the resol and Novolac Resins.

In the next step, this thick solution was prepared (a little viscous) into a silicon mold of :22cm³ size (11×1×2), then we placed in convectio oven from (PROTHERM) at 120°C for 2 hours and half.

After takin git out from the oven, the sample were removed for 15min it out the mold, we recorded its new weight so that we could know a solid content parcentage and do our analysis. Now we are going to repeat the same expriment using only 30g of Phenol (without SAWDUST which contain O-H×5 links) and the same steps then place it in the oven, after we record its new weight.

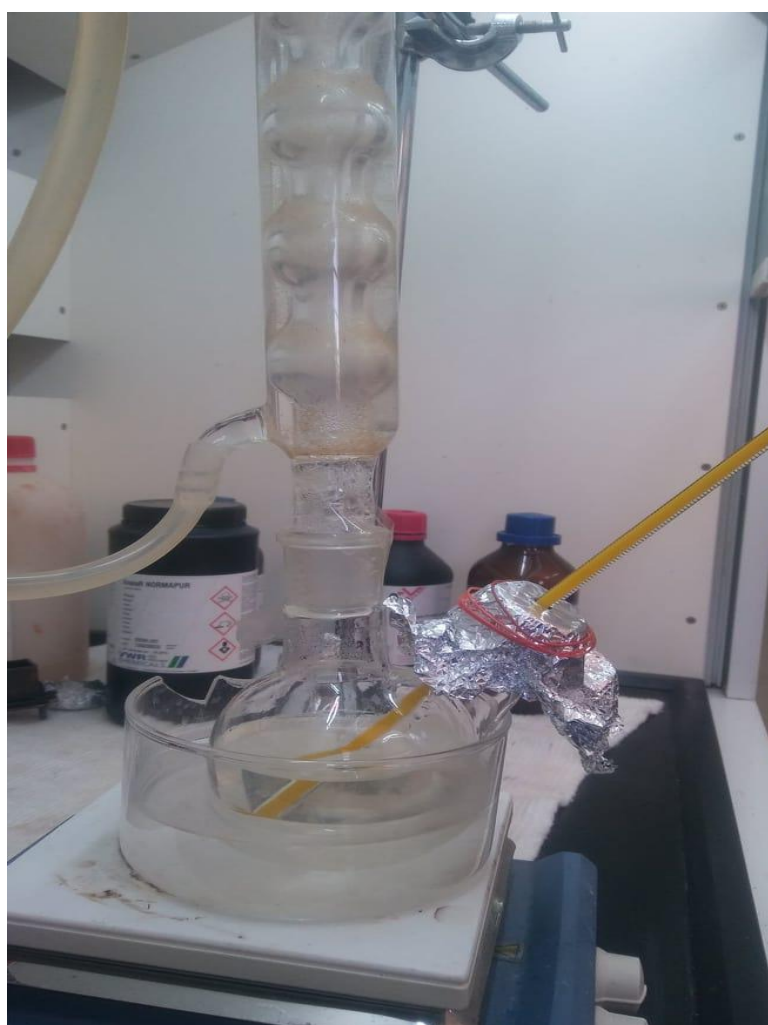


Figure 8: Exprement fabrication of resol

Characterisation

II.3) Degree of cure

Have puting 3,62g of Resol (with wood) into 31,63ml of Toluen solvent, we record its weight each 24/48/72/96/120/144/168 hours in order to know its chemical resistance against solvents. We do the same steps with resol without wood.

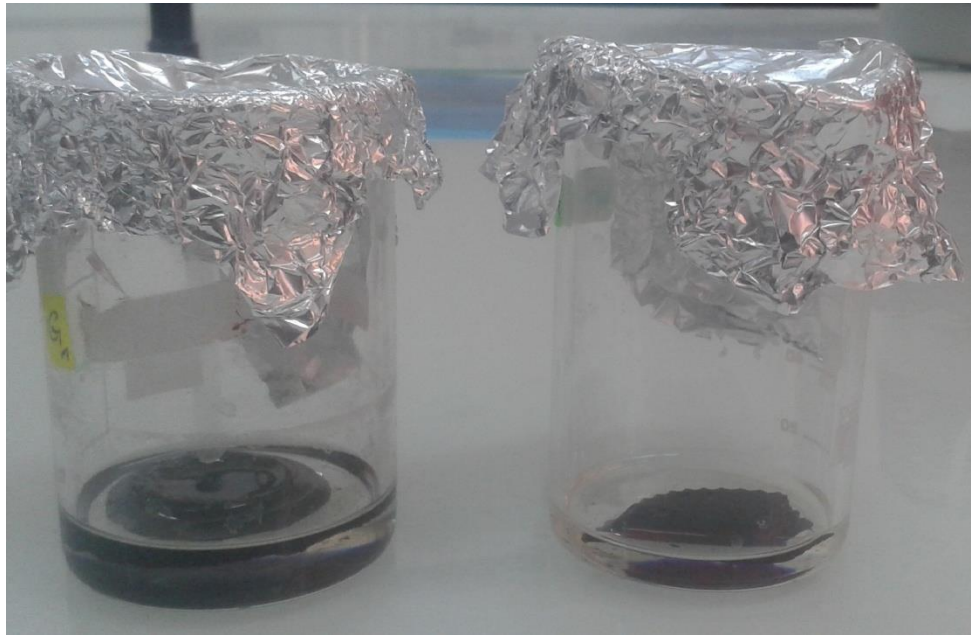


Figure 9: Resol in toluene

Mechanical properties

We are interested in the toughness of this fragile materials there for we based (focus) our investigation on choc test.

II.4) choc test (charpy)

The Charpy impact test, also known as the Charpy V-notch test, is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's notch toughness and acts as a tool to study temperature-dependent ductile-brittle transition. It is widely applied in industry, since it is easy to prepare and conduct and results can be obtained quickly and cheaply. A disadvantage is that some results are only comparative. The Test was developed around 1900 by S.B. Russell (1898, American) and Georges Charpy (1901, French). The test became known as the Charpy test in the early 1900s due to the technical contributions and standardization efforts by Charpy. The test was pivotal in understanding the fracture problems of ships during World War II. Today it is utilized in many industries for testing materials, for example the construction of pressure vessels and bridges to determine how storms will affect the materials used.

Quantitative results

The quantitative result of the impact tests the energy needed to fracture a material and can be used to measure the toughness of the material. There is a connection to the yield strength but it cannot be expressed by a standard formula. Also, the strain rate may be studied and analyzed for its effect on fracture. The ductile-brittle transition temperature (DBTT) may be derived from the temperature where the energy needed to fracture the material drastically changes. However, in practice there is no sharp transition and it is difficult to obtain a precise transition temperature (it is really a transition region). An exact DBTT may be empirically derived in many ways: a specific absorbed energy, change in aspect of fracture (such as 50% of the area is cleavage), etc.[14]

Qualitative results

The qualitative results of the impact test can be used to determine the ductility of a material. If the material breaks on a flat plane, the fracture was brittle, and if the material breaks with jagged edges or shear lips, then the fracture was ductile. Usually a material does not break in just one way or the other, and thus comparing the jagged to flat surface areas of the fracture will give an estimate of the percentage of ductile and brittle fracture.

Impact test results on low- and high-strength materials

The impact energy of low-strength metals that do not show change of fracture mode with temperature is usually high and insensitive to temperature. For these reasons, impact tests are not widely used for assessing the fracture-resistance of low-strength materials whose fracture modes remain unchanged with temperature. Impact tests typically show a ductile-brittle transition for low-strength materials that do exhibit change in fracture mode with temperature such as body-centered cubic (BCC) transition metals. Generally high-strength materials have low impact energies which attest to the fact that fractures easily initiate and propagate in high-strength materials. The impact energies of high-strength materials other than steels or BCC transition metals are usually insensitive to temperature. High-strength BCC steels display a wider variation of impact energy than high-strength metal that do not have a BCC structure because steels undergo microscopic ductile-brittle transition. Regardless, the maximum impact energy of high-strength steels is still low due to their brittleness. [15]

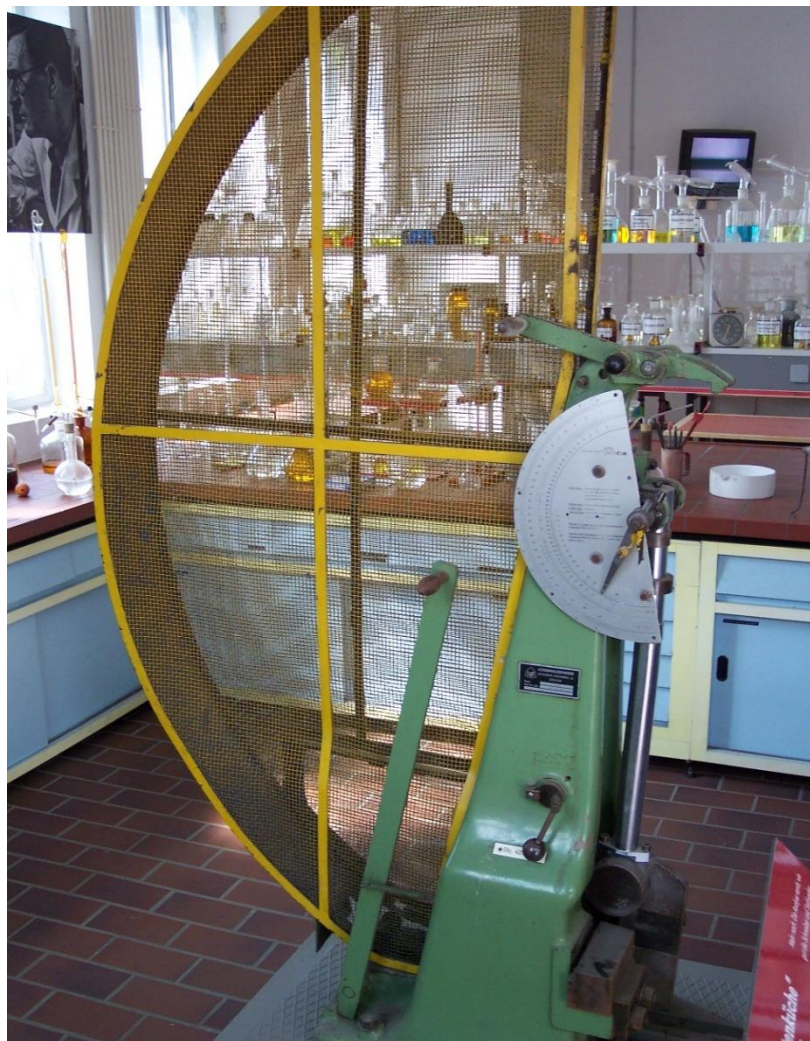


Figure 10: A choc test (Charpy impact) machine. [12]

II.5) Electrical test

Measurements of electrical resistivity were performed in situ during the heat treatment from room temperature up to 1000°C. The heat treatment was done in a EDG furnace, model PHYWE, under nitrogen atmosphere, gas flux of ~2 L/min, and heating rate of 3°C/min. The samples were fixed by four equidistant (30 mm) steel screws used as probes for current and potential. Electrical Kanthal A1 wires of about 0.5 mm diameter were fitted to the screws, as shown by [Figure a, b](#). The experimental set-up of the electrical resistivity measurements, as well as the specimens, are shown in [Figure a, b](#), respectively.

In order to obtain pyrolysed composites at progressive levels of heat treatment, samples were pyrolysed, under nitrogen atmosphere, at a heating rate of 3°C/min, from 300°C up to 1000°C, at intervals of 100°C. After pyrolysis at each temperature level, sample cross section were sectioned and mounted in a resin. The polishing was accomplished by grinding in SiC abrasive paper and diamond polishing with synthetic wool, according to standard materialographic sample preparation procedures. Cross section of the composites was examined by a Carl Zeiss AxioImager A2m optical microscope, under 50x magnification. Representative figure were taken in five different regions of the cross section from each sample. figure analysis was done by a sampling procedure were a number of images acquired from each specimen were chosen in order to obtain a representative view of the whole polished sample. The figures recorded were treated in order to segment the pores and microcracks (dark areas) in the figure. The figure analysis procedure consisted in: (1) contrast enhancement, (2) conversion to 8 bits gray scale (256 gray shade levels), (3) threshold adjustment, (4) figure treatment, in order to measure dark feature areas. The concept of threshold allows identification of pores and microcracks from the background determining the amount and area fraction. A statistical analysis was conducted to get the mean area of dark fields and standard deviation for each set of figure. This analysis allows following the microstructure development during pyrolysis of the carbon fiber/phenolic resin composite.

Volume fractions of fiber, matrix and pores were calculated by using simple micromechanic equations. Thus, the volume fractions of fiber, matrix and pores can be obtained by Equation 2.

$$V_i = \%M_i * \rho_c / \rho_i. \text{Equation 2}$$

Where :

V_i = volume fraction of fiber or matrix;

M_i = weight (mass) fraction of fiber or matrix;

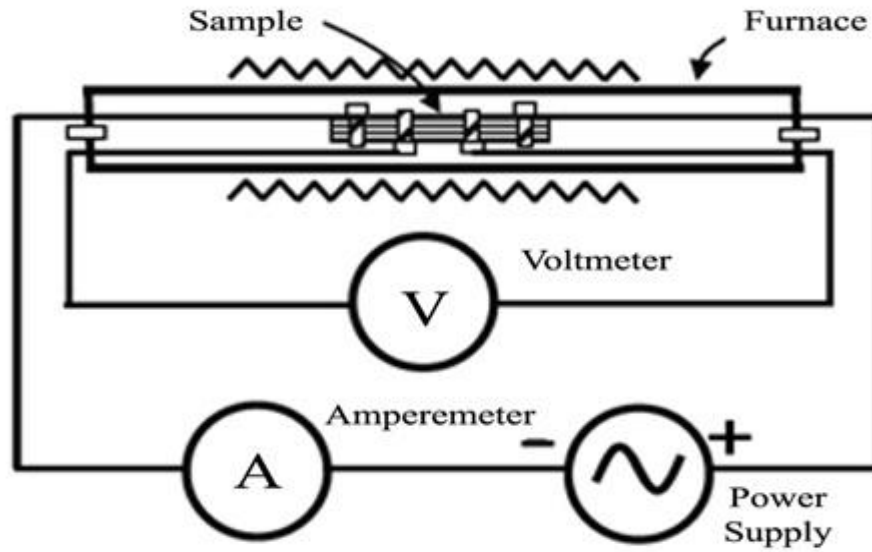
ρ_c = composite density ;

ρ_i = density of fiber or matrix.

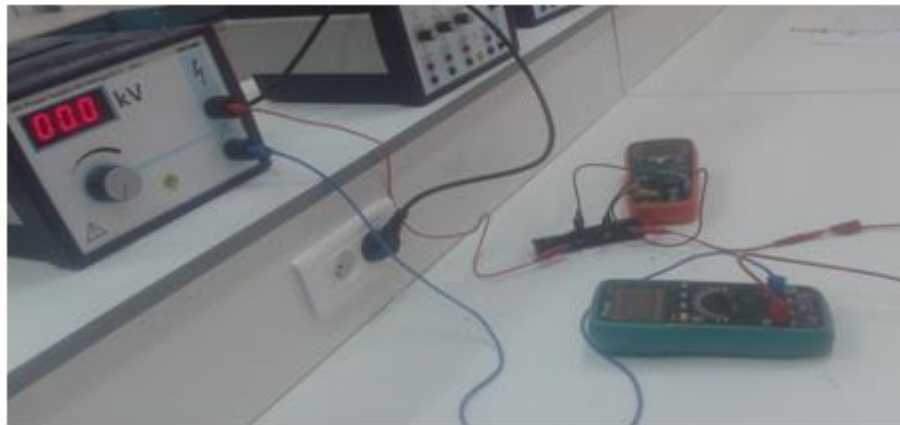
The pore volume fraction can be estimated by calculation from Equation 3.

$$V_{\text{pores}} = 1 - (V_{\text{fiber}} + V_{\text{matrix}}) \quad \text{. Equation 3}$$

A Labview subroutine was implemented to obtain data of electrical resistivity, simultaneously to the heat treatment of specimens. Labview is called virtual instrument since its appearance emulates the operation of physical instruments, such as oscilloscopes and multimeters. The input parameters were the dimension of the specimen and multimeters readings (voltage and current), in order to obtain results of electrical resistivity. Five readings were obtained at programmed temperature interval during heat treatment. In this work two multimeters model EXTECH (voltage source and current source) were used. [16]



(a)



(b)

Figure 11: (a) Schematic of the set-up of electrical resistivity measurement, (b) carbon fiber/phenolic composite sample showing equidistant attached screw terminals.

II.6) The density

have puting a 12,67g of resol (with wood) in a beaker and we immerse it in water in order to know its volume.

Chapter III: Result and discussion

III.1) degree of cure

Table 3: Variation weavy of resol(with wood)in 20,85ml touluen

Date	26/5/19	27/5/19	28/5/19	29/5/19	30/5/19	02/5/19
Hours	0	24	48	72	96	168
Weight	3.62g	4.02g	4.11g	4.01g	4.01g	4.01g

Table 4: Variation weavy of resol(without wood) in 31,65ml touluen

Date	19/5/2019	20/5/2019	21/5/2019	22/5/2019	23/5/2019	26/5/2019
Hours	0	24	48	72	96	168
Weight	2,37g	2,47g	2,49g	2,51g	2,43g	2,43g

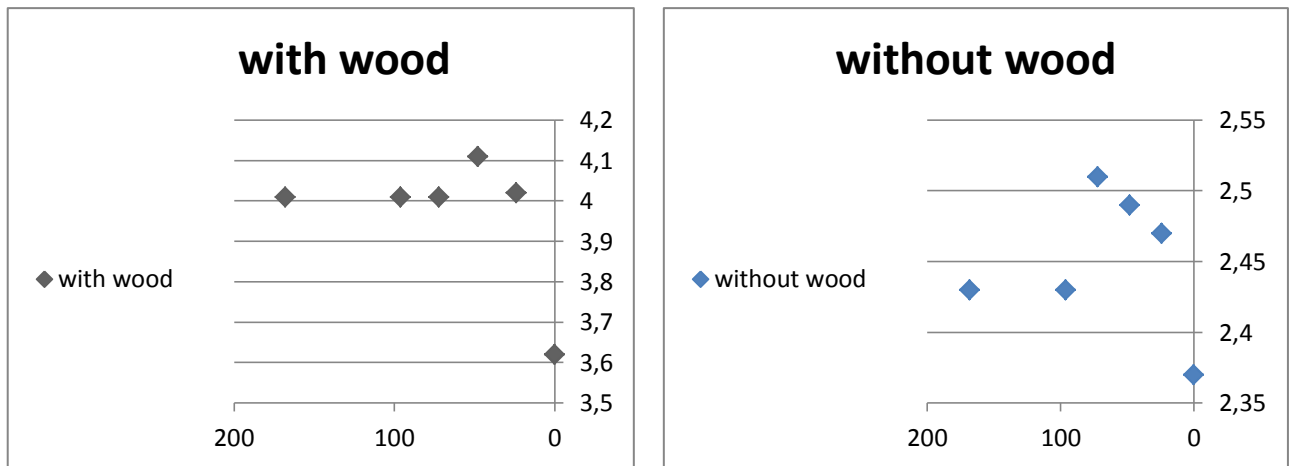
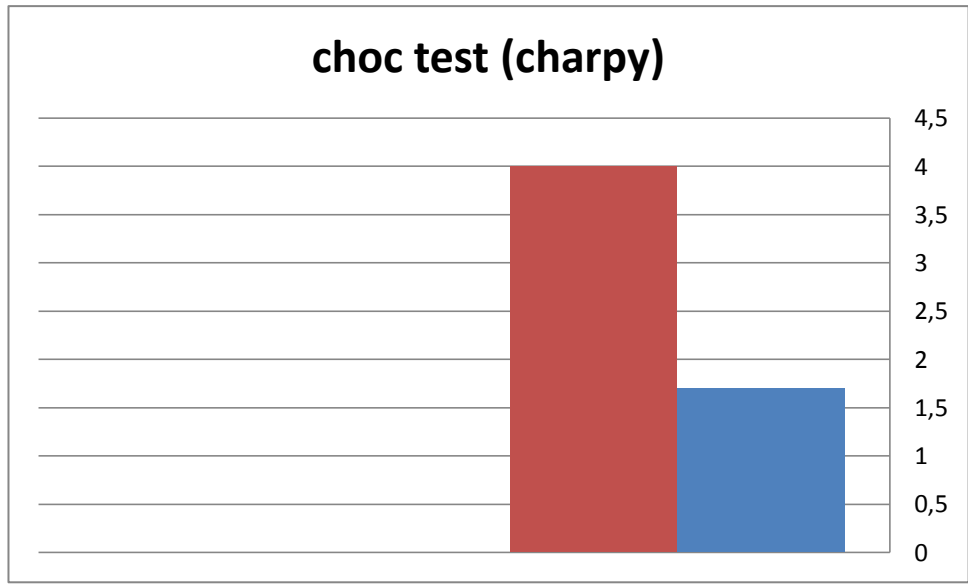


Figure of Hystogramme presented deffernce between a sample with wood and without.

Discussion:

We note that the weight of both samples of Resol after immersion in the solvent of the Toluene increase over time because the Toluene are placed in the pors in each of the samples Risol and then proved in a certain weight until the absorption of the amount of Toluene.

III.2) choc test (charpy)



**Figure of Hystogramme presented the choc test deffernce
(Red=without wood; blue=with wood; unite=joul)**

Discussion:

We note that the sample containing wood was the force that applied and broken it is: 1.7 Joule and the sample which does not contain the components of the wood was: 4 Joule. we concluded that the sample that does not contain wood stronger than the other sample that contains wood perhaps because The wood is a Deposition in an area at the expense of another, and there is no mixing between the the ingredients , and the sample that does not contain wood whose components are well mixed and balanced.

III.3) Electrecal test

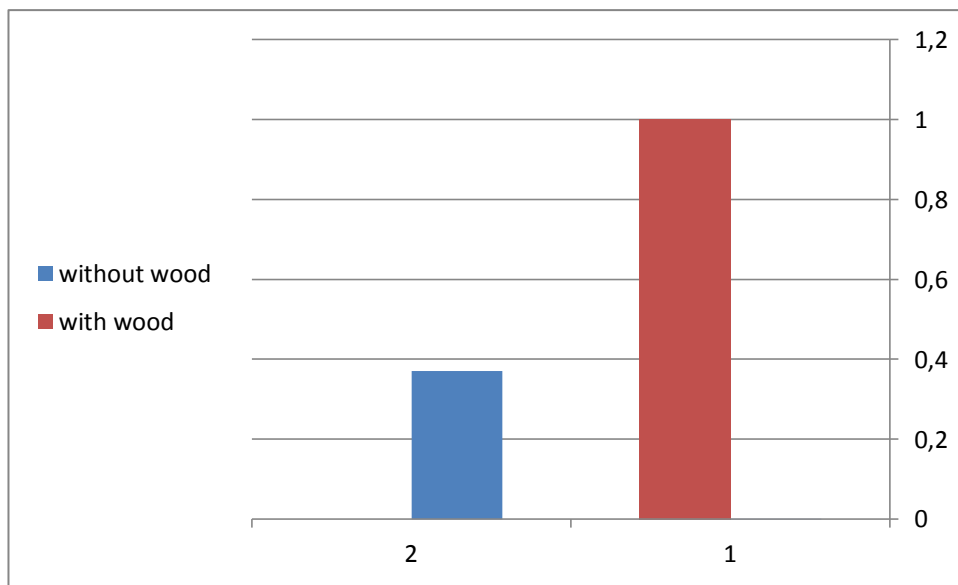


Figure of Histogramme presented defference between a sample with wood and without for Electrical Test

Discussion:

We note that the sample containing wood is more resistant to electricity than the sample without contain it, because the wood particles are excellent insulation for the electricity, and the fear of saturation of the wood particles with water because it can become a passage of the electricity then.

III.4) the density

We find the sample: 19ml , we conclude that the density of resol (without wood) is: $\rho=m/v=0.669\text{g/ml}$, and the density of resol (with wood) is: $\rho=0,81\text{g/ml}$.

Table 5: the density of resol

	With wood	Without wood

The density	0.81g/ml	0.669g/ml
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Discussion:

We Note that the density of the sample containing the wood is higher than the sample without contain it, because the wood contains a lot of the links of the O-H, while in the phenol there is only one link and thus increase the density in the sample containing wood.

III.5) Conclusion

This experimental work offers us the possibility to make an electrical insulating materials using a phenolic resin. It showed also the potential of using the wood as a reinforcement to boost this property. This work also needs further improvement concerning the improvement in the formulation through variation of wood content and curing temperature in the oven.

III.6) Bibliographics references

- [1] Pam Hatchfield, Pollutants in the Museum Environment, Archetype Press, London, 2002
- [2] G.S.Brady, Materials Handbook, McGraw-Hill Book Co., New York, 1971 p. 598
- [3] J.A. Brydson, in Plastics Materials (Seventh Edition), 1999
- [4] A. Knop and L.A. Pilato, Phenolic Resins, Springer, Berlin, Germany, Heidelberg, Germany and New York, NY, USA, 1979.
- [5] W.D. Cook, G. P. Simon, P.J. Burchill. M. Lau, T.J. Fitch, Journal of Applied Polymer Science, 1997, **64**, 769.
- [6] Encyclopedia of Polymer Science and Engineering, Volume 6, 2nd Edition, Eds., H.F. Mark and J.I. Kroschwitz, Wiley, New York, NY, USA, 1991, p.322.
- [7] Handbook of Thermoset Plastics, 2nd Edition, Ed., S.H. Goodman, Noyes Publications, Park Ridge, New Jersey, USA, 1998.
- [8] C.A. Pryde, Journal of Polymer Science: Polymer Chemistry Edition, 1989, **27**, 711.
- [9] P.L. Dynes, T.T. Liao, C.L. Hammermesh and E.E. Witucki in Polyimides: Synthesis, Characterisation and Applications, Ed., K.L. Mittal, Plenum, New York, NY, USA, 1984, 311-326.
- [10] Handbook of Thermoset Resins,Debdatta Ratna, iSmithers – A Smithers Group Company, Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom.

- [11] Chemistry and Technology of Cyanate Ester Resins, Ed., I. Hamerton, Blackie Academic & Professional, Chapman & Hall, London, UK, 1994.
- [12] *Meyers Marc A; Chawla Krishan Kumar (1998). Mechanical Behaviors of Materials. Prentice Hall.*
- [13] Hoadley, Bruce. Identifying Wood: Accurate Results With Simple Tools. Newton, CT: Taunton Press, 1990.
- [14] Cedric W. Richards (1968). Engineering materials science. Wadsworth Publishing Company, Inc.
- [15] The Design and Methods of Construction Of Welded Steel Merchant Vessels: Final Report of a (U.S. Navy) Board of Investigation (July 1947). "Welding Journal". **26** (7,). Welding Journal: 569.
- [16] Tennison SR. Phenolic-resin-derived activated carbons. Applied Catalysis A: General. 1994; 173(2):289-311.

III.7) Annexes



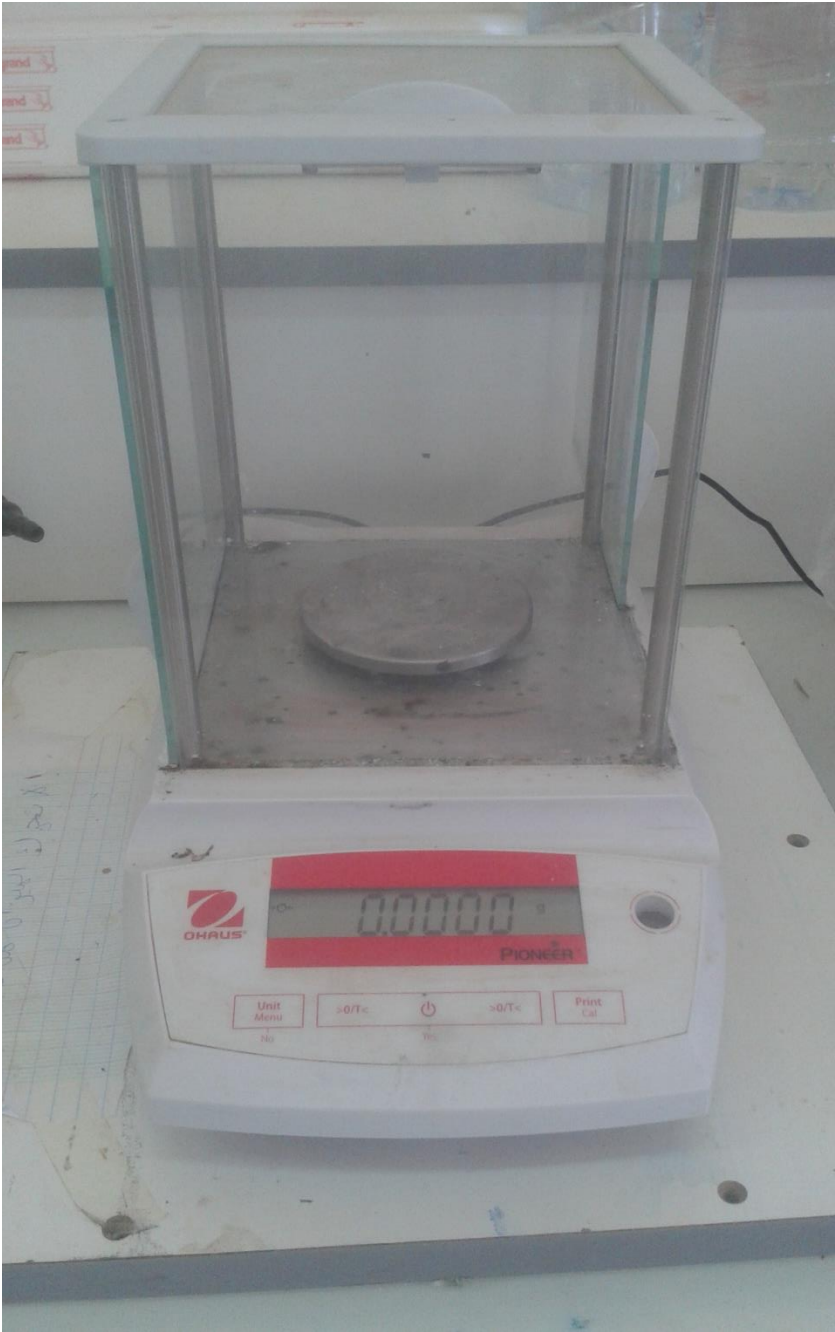
Annexe 1: Thermique oven



Annexe 2: Heat and steering plate



Annexe 3: Power supply



Annexe 4: Balance



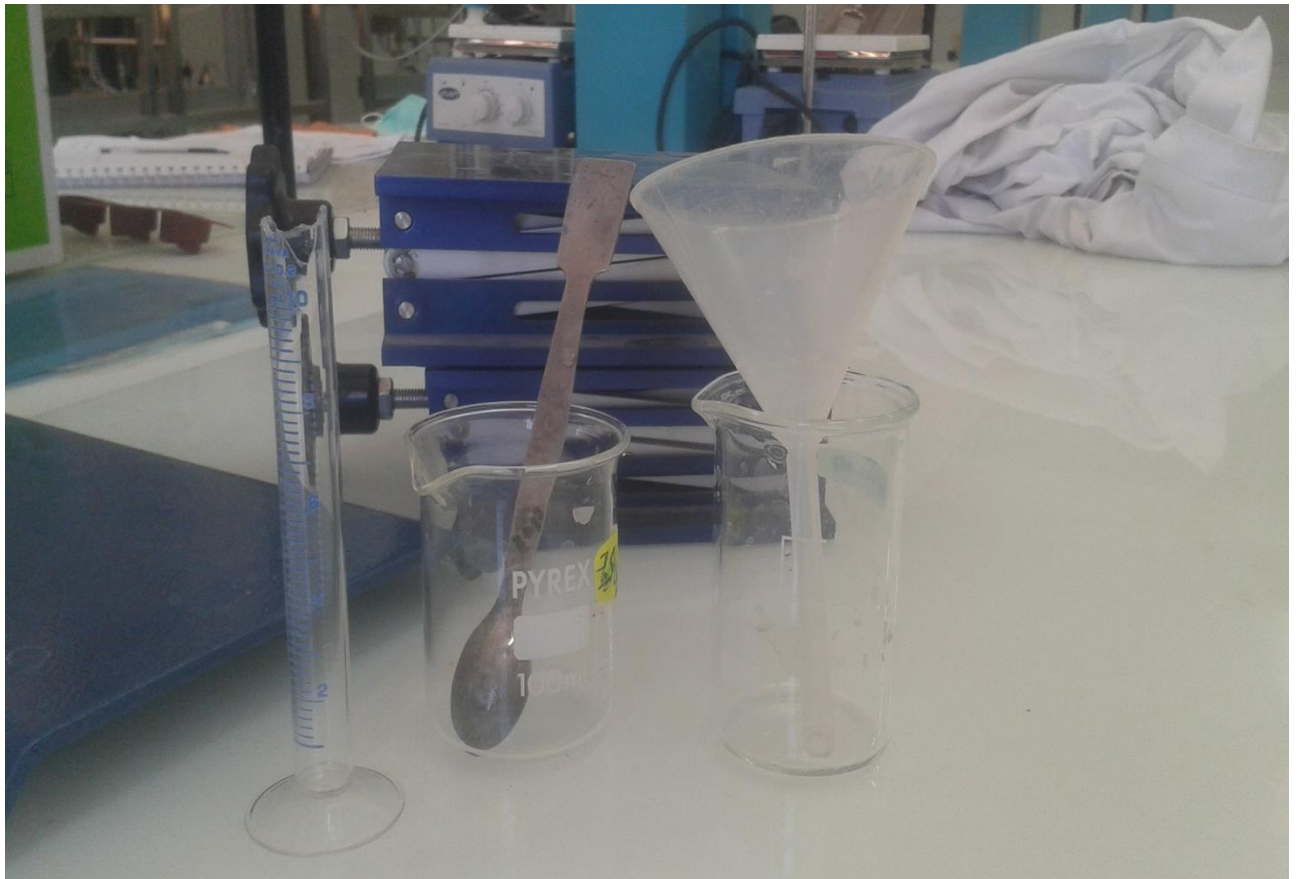
Annexe 5: Mold



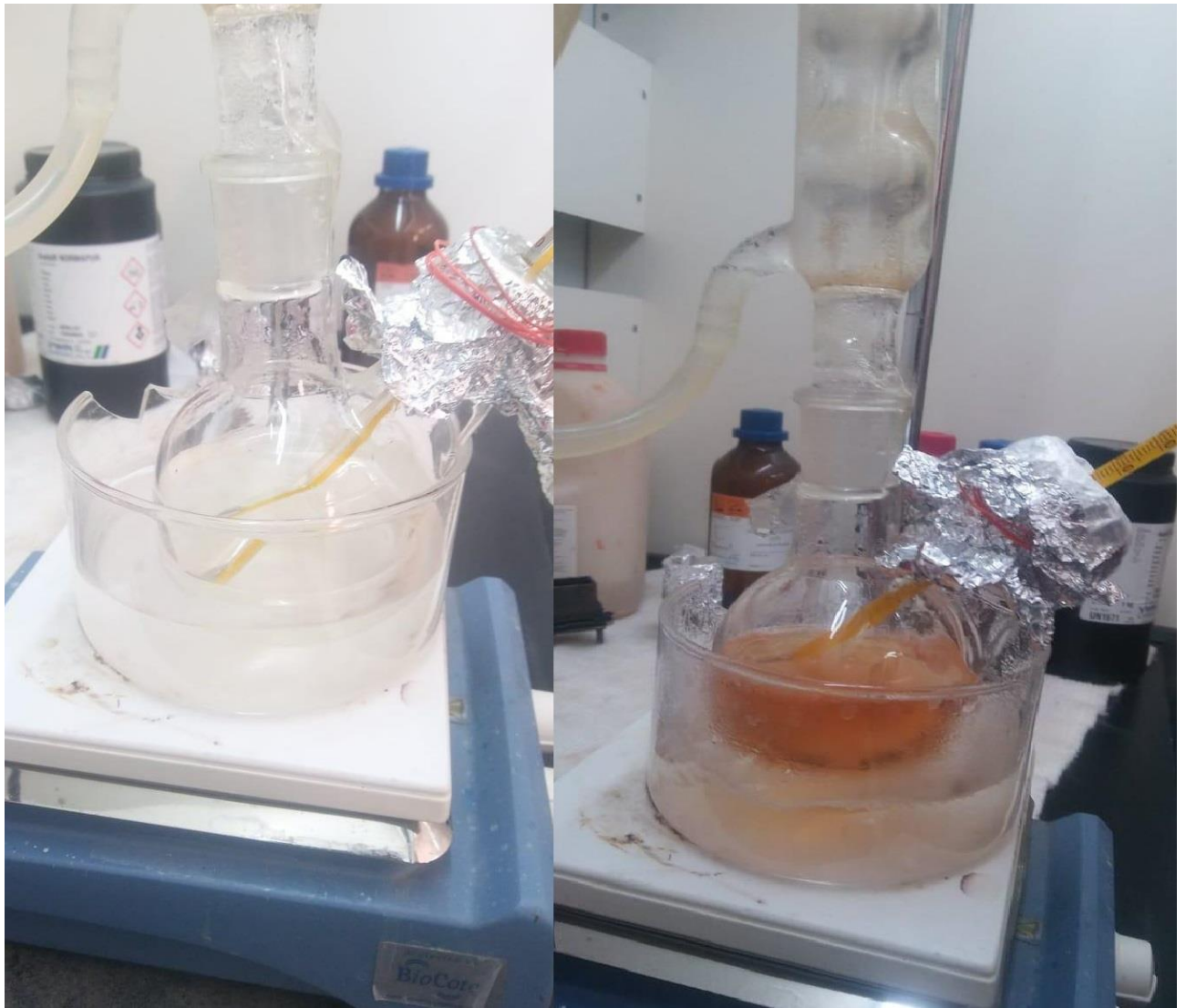
Annexe 6: a Fume hood



Annexe 7: The bera test sieves



Annexe 8: The verrerai



Annexe 9: the Resol before and after



Annexe 10: a Sample of Resol Phenolic