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## Abstract

Different carbon-based materials are used to tailor the properties of composites. However, there is a trend to replace the expensive carbon fillers with a cheap alternative that is not only abundant in nature but can also be produced comparatively faster than the ones that has maximum share in today's market. Now the scientists also made resins that are biodegradable, so when both the resins and fillers are biodegradable this not only address the issue of cost but also that of recycling as well. The increase in environmental consciousness, energy crisis, and strict environmental regulations are shifting the focus towards cheap and sustainable composites. In this study the resin we use is not readily biodegradable, however, the reinforcement material is a green material. By and large the studies have found that the fillers in conjunction with resins has improved mechanical properties. Since there are numerous types of feedstocks for the fillers and various pyrolysis technologies and conditions, the properties of biochar (BC) vary widely, which in turn alter the properties of the end product, therefore there is a lot of work needed to be done in this area. This study will be supportive for the future work in this area as it is considering a vast range of olive BC and weight percentage of fillers.

The aim of this study is to investigate different mechanical properties (such as ultimate tensile strength, Young's modulus and toughness) of polymers added with olive BC. It discusses how the properties of composites depend on the conditions at which BC is obtained as well as on the weight percentage of the filler.

The BC was produced by the thermal decomposition of the olive feedstock in a closed heated chamber under the supply of nitrogen gas, at maximum temperature i.e. 400 °C, 600 °C, 800 °C, and 1000 °C and at different heating rates i.e. 5 °C/min, 15 °C/min, and 50 °C/min.

Different batches of samples were prepared with different weight percentage of fillers (0.5 wt.%, 1 wt.%, and 2 wt.%).

The study includes a discussion on the epoxy resin and its type, it also discusses the preliminary characterization of olive and preparation of BC.

The morphology of BC obtained is also studied with the aid of FE-SEM. The study of BC through FE-SEM gives an insight to observe the surface structure and minerals distribution of BC. The surface morphology changes greatly from 400°C to 1000°C.

Last but not least, there is a discussion on each mechanical property for each batch supported by the graphs of the testing results obtained via Q-Test-10 Mechanical apparatus.

## **1** Introduction

#### 1.1 Biochar

BC is the carbon-rich product obtained when biomass, such as wood, manure, or leaves, is heated in a closed container with little or no available oxygen. In more technical terms, BC is produced by the so-called thermal decomposition of organic materials under limited supply of oxygen  $(O_2)$ and at relatively low temperature (Lehmann 2015).

The property of BC produced is much dependent upon the composition, type of biomass, and the conditions at which biomass is carbonized (Anexo 44 2002). The precursors for BC are woodchips, wood pellets, rice husks, bamboo tree, beech tree, cotton stem, wheat straw (without leaves), corn stem (without leaves), peach branch, walnut shell, yak manure, wood sawdust, maple to name a few. BC has numerous applications in diverse areas because they possess versatile physio-chemical properties. Some areas of applications are energy production through combustion, activated carbon, carbon sequestration, char gasification, soil remediation and bio chemistry (Nanda et al. 2015).

The heating rate and pyrolysis temperature are the factors that determine the properties of BC, such as surface area, porosity, mineral phases, carbon yield, conductivity etc. (Angin 2013).

BC is obtained at low temperature (100°C<T<600°C) of pyrolysis show higher carbon yield, better electrical conductivity, comparatively higher level of volatile, and higher cation exchange capacity as compared to the BC produced at higher temperature. Whilst on the other hand the BC obtained at higher temperature of pyrolysis preserve large surface area, micro-porosity and greater amount of aromatic carbon (Ronsse et al. 2013).

Different functional groups and their amounts in BC are function of the processing conditions and feedstocks. For example, the amount of carboxylic and phenolic groups in BC obtain from crop straws decreases by rising the temperature of pyrolysis from 300°C to 700°C (Yuan et al., 2011a). Yuan and Xu (2012) also observed that the carboxylic groups were less abundant than the phenolic groups in BC derived from crop residues, and the contents of both groups varied with the type of crop residue. BC derived from wheat, canola and rice chaff at 350°C had comparatively higher contents of the carboxylic group, as compared to BC generated from legume straws of fava

bean, pea, and mung bean at the same temperature which had relatively low contents of this group (Yuan and Xu, 2012). (Deem, Crow, and Systems 2017)

BC is mainly composed of carbon with traces of sodium, calcium, barium, magnesium and potassium. BC possesses micro or meso pores which depends on the feedstock and conditions at which pyrolysis is carried out. BC has high thermal stability and carbon yield. It has versatile structure, reactivity, and elemental composition. One of the advantages of BC is that it is a cheap filler to reinforce polymer composites.

BC composition is highly heterogeneous, containing both stable and unstable components. Its heterogeneous chemical composition results in complex surface chemistry that affects the way it interacts with a wide range of organic and inorganic compounds in the environment (Deem et al. 2017).

Summarizing, BC is a material that has advantages because of the origin of its precursor from the nature which is not only renewable but also available in abundance.

#### 1.2 Epoxy Resin

Epoxy resins are one of the most versatile classes of thermoset materials widely used in structural and particularly composite application. It was 1940 when for the first time the commercial interest in epoxy resins arose. The superiority of epoxies over the thermosets available at that time (mainly phenolic and amino resins, which both produce water as an undesirable condensation product) was soon evident. Epoxy offers excellent properties as compared to other thermoset resins (Anon n.d.). The resins possess two or more ring-like epoxy groups in the monomer. The group shown in Fig.1.1, is alternatively referred to as epoxide or oxirane which may lie within the body of the molecule but is usually terminal.

Figure 1.1

Most of commercial resins are derived from petroleum and are themselves the result of a reactive process involving epoxide units. Epoxy resins are quite stable at room temperature and gain their ultimate performance characteristics only when reacting with curing agents such as polyamines, aminoamides and phenolic compounds. The most common epoxy resins are based on reacting epichlorohydrin with Bisphenol A. This reaction transforms the basic building blocks into a different chemical substance called Bisphenol A diglycidyl ether, which is a low molecular resin more commonly known as BADGE or DGEBA, shown in the Fig.1.3.



Figure 1.2 Diglycidyl ether of bisphenol A (DGEBA)

Epoxy resins are measured according to their epoxide content, also known as epoxide number. The state of the resin will change depending on its epoxide number (Anon n.d.). Low molecular epoxy resins with a molecular weight of 380 (EEW)<sup>\*</sup> will be fluid at room temperature, while resins with a molecular weight of 1000 (EEW) and beyond will be solid. This number is also useful to calculate the amount of hardener to use when curing the resin. Low molecular epoxies can be handled without solvents and are used for castings, thick coatings, gap-filling glues etc. High molecular epoxy resins can be dissolved in organic solvents to become manageable and are mostly used for paints and lacquers. In their solid form they are often employed as powder coatings. Epoxies are amorphous resins that can be tailored, through the use of different prepolymers to achieve glass transition temperatures (Tg)<sup>\*\*</sup> in a broad range, depending on the choice of constituents. The properties can range from tough and resilient to hard and strong. The modulus of the material above its Tg is typically several orders of magnitude lower than its value below the Tg, therefore it is important to consider this factor when selecting epoxy resin (Anon n.d.).

<sup>\*</sup>Epoxide Equivalent Weight (EEW) of epoxy resin.

<sup>\*\*</sup> The Glass Transition Temperature (Tg)

As said above the commonly used resin is diglycidyl ether of bisphenol A (figure 1.2). Its Tg is in the from 101°C to 205°C (Plazek, Donald & C. Choy, I. (1989)). It accounts for over 70% of all epoxy usage. The epoxy group forms cross-links by a condensation mechanism with several hardener systems, of which secondary amines and acid anhydrides are the most important. With a suitable catalyst, such as boron trifluoride or a tertiary amine, epoxies can also polymerize by themselves. Epoxies were the first commercial thermosets to allow chain extension and cross-linking to occur without the elimination of condensation products such as water. They also exhibit lower-curing shrinkage than many other types of thermoset.

Figure 1.3 shows that composite materials has a great amount of share in epoxy resin market. This sector is expected to expand as a result of the new generation of lighter and more fuel-efficient aircrafts. The fuselage of Airbus A380 is manufactured from the multilayer metal laminate, GLARE (Glass Laminate Aluminum Reinforced Epoxy).



Figure 1.3 Share of the world markets for epoxy resin by value

On top of the resins based on bisphenol A discussed earlier, a number of other resins containing epoxy groups are also available which can be treated in two main groups:

- 1. Other glycidyl ether resins
- 2. Non-glycidyl ether resins

#### **1.3 Composite Materials**

Composites materials are made by combining two or more materials having significantly different properties. The material thus obtained have unique properties unattainable by the individual constituents. Composites are designed with a view to produce materials whose properties are tailored according to the requirements. Composites have introduced an extraordinary flexibility to design engineering and forcing the designer analysis to create a different material for each application as she/he pursues savings in cost and weight.

Composite materials were known to humans from the very early age in the form of buildings construction materials such as bricks (prepared by mixing straw and mud). Another known composite at ancient times was the concrete, which is a mix of sand, cement, gravel, metal rods, gravels or stones. Such concretes were called reinforced concrete (Rsc n.d.).

One of the first modern composite materials was fiberglass, which is still widely used for sports equipments, boat hulls, automobiles, and building panels.

Some other advanced composites are made of using carbon fibers instead of using glass, which are stronger and lighter than fiberglass, but the disadvantage is that they are expensive to produce.

Many composites used today are leading materials technology with cost effectiveness and performance and have numerous applications both in engineering and medical fields.

Carbon nanotubes (CNTs) are also used to make composites which are even stronger and lighter than the composites that are made with ordinary carbon fibers, but like fiberglass they are also expensive to produce. They offer possibilities of producing lighter parts in automotive and aerospace industry which eventually will reduce the fuel cost.

The role and importance of composites in aerospace industry can be guessed from their increase usage in the new coming aircrafts. A320, the first aircraft to go into production with an all-composite tail, about 13% by weight of the wing on the A340 is composed of composite materials. A380 the center wing box will weigh around 8.8 tons, of which 5.3 tons are composite materials.

More than 20% of the A380 is made of composite materials (Pora 2001). Besides Airbus, Boeing 787 has composites in the fuselage, windows, wings, tails, stabilizers etc. resulting in 50% in composites by weight.

The selection of composite technologies is also linked to cost studies. The biggest advantage of modern composites is that they are both strong and light weights. Proper combination of matrix and reinforcement will yield a composite that will meet the desired demand.

Last but not the least, the subject of composite materials is truly an inter and multidisciplinary one. People working in fields such as metallurgy, materials science, engineering, chemistry, chemical engineering, solid mechanics, and fracture mechanics have made important contributions to the field of composite materials.

#### 1.4 Area of Research Activity

Studies have found that the carbon fillers in conjunction with resins have improved mechanical properties. Different carbon based materials are used to tailor the properties of composites. Fillers such as fiber glass, carbon fillers, and carbon nanotubes improve mechanical properties of the composites but they are expensive. The increase in environmental consciousness, energy crisis, and strict environmental regulations are shifting the focus towards cheap, sustainable, and green composites. The scientists have discovered a range of new thermoset resins that are made from renewable raw materials and are fully biodegradable. Green bio-composites is a new subject and the unavailability of vast knowledge is a challenging obstacle.

In this study we investigate different mechanical properties of the polymer composites using olive biochar as a filler. The filler used in this study is cheap as well as eco-friendly because more than 80% of its content is carbon that would have been released to the atmosphere otherwise.

Mechanical properties of polymer composites using biochar depend on various factors such as type of feedstocks, different pyrolysis technologies, and different pyrolysis conditions. Our work is limited to only one feedstock (olive), different maximum temperature of pyrolysis, and heating rates.

#### 2. Experimental Setup

#### 2.1 Materials and Apparatus

The following materials and apparatus were used in conducting this study.

- Epoxy Resin LPL Component-A , Chemical name: Epoxy Resin
- Epoxy Resin LPL Component-B, Chemical name: Amine Hardener
- ✤ Olive Wasted Woods
- ✤ Carbolite Tube Furnace (TZF12/65/550)
- ✤ Weighing Balance
- ✤ Sieves
- Digital Vernier Caliper
- Plastic Bottles (for keeping powder BC)
- ✤ Flasks
- Sonicator
- Molds
- Oven
- ✤ FE-SEM
- ✤ Raman
- MTS Q-test-10 Mechanical tester

#### 2.1.1 Epoxy Resin

The epoxy resin used in this study has a business name Cores Srl. It is comprised of two agents that are the glycidil monomer (component A) and a mix of amines (component B).

#### 2.1.1a Component A

The chemical name of the component A is epoxy resin. It has a reaction product Bisphenol A Epichlorohydrin ((C15-H16-O2.C3-H5-Cl-O)x-), having initial boiling point greater than 200°C and ignition temperature greater than 300°C. There are no particular risks of reaction with other substance and is chemically stable during normal conditions of use. It is not readily biodegradable.

On the basis of available data the epoxy product does not contain Polybutylene Terephthalate (PBT) and Very ersistent and Very Bioaccumulative (vPvB).

#### 2.1.1b Component B

Epoxy resins can have different properties as it is combined and cured together with different curing agents. The curing agent (component B) used in this study is an Amine Hardener. Amine compounds are classified into primary, secondary, and tertiary amines. These amines are also called mono-amine, di-amine, tri-amine, or poly-amine based on the number of amines. Aromatic amine has weaker basicity than aliphatic amine and slowly cures at room temperature due to steric hindrance by the aromatic ring (Hara 1993). They are classified into aliphatic, alicyclic, and aromatic amines according to the types of hydrocarbons involved. They all are curing agents for epoxy resins. The cured resin has an excellent properties. Aliphatic amine is curing agent for epoxy resin and it is able to cure at room temperature. Aromatic amine has been developed to attain greater chemical resistance and thermal resistance than aliphatic amines.

#### 2.2 Methods

In this work the samples of neat epoxy and epoxy added with BC were prepared with different percentages of fillers, obtained at various temperatures, heating rates, and all cured at same temperature (70°C) for 4-hours to investigate their mechanical properties.

The procedure of making and testing of samples is discussed below;

- Pyrolysis
- BC Preparation
- Sonicator
- Sample Preparation
- FE-SEM
- Raman
- MTS Q-test-10 Mechanical Tester

#### 2.2.1 Pyrolysis

Pyrolysis heats up the feedstock in absence of oxygen. The process irreversibly changes the physical and chemical characteristics of the feedstock. The process was carried out in a Carbolite tube furnace (TZF12/65/550).

#### 2.2.2 Biochar

The dried raw feedstock of olive was cut into suitable pieces in accordance with the size of furnace tube. The pieces were put in the tube and air tightened. The maximum temperature and the heating rate of the furnace were set in each pyrolysis process. The BC was produced by the thermal decomposition of the olive feedstock in a heated closed chamber under the supply of nitrogen gas, at different maximum temperatures i.e. 400°C, 600°C, 800°C, 1000°C and each set at different heating rates i.e. 5°C/min, 15°C/min, 50°C/min.

After reaching maximum pyrolysis temperature, the furnace was kept at the same maximum temperature an hour and then BC was cooled in the furnace with continuous supply of  $N_2$ . After cooling the furnace was turned off, the supply of  $N_2$  was stopped, BC was kept with-in the furnace and removed the next day. The BC obtained was weighted, grinded into powder, sewed, and particles having size below 100µm were used for composite preparation.

#### 2.2.3 Sonicator

For mixing, appropriate dispersion, and to further reduce the particle size of the powder of filler in the matrix, Elmasonic S15H Sonicator (vcx500 and vcx750) was used. Before making the samples of this work, several tests were conducted to set a suitable pulsing time and to have an idea of rise in temperature during sonication process. Before every test the room temperature was recorded i.e. at time t=0. Water was used as a coolant. The pulsing time for ON and OFF cycle was set at 30s and 10s respectively. A total of five tests were conducted-three on water, and one test on each; monomer alone and monomer mixed with filler. In the three cases of water (water only without using magnetic stirrer, water only using magnetic stirrer, water mixed with filler using magnetic stirrer) the rise in temperature was slow. As shown in the graph (figure 2.1) it reaches 40°C in the first 10-15 minutes and after that it is rising slowly. In the other two cases (monomer alone and monomer mixed with filler), it was noticed that during the first 10-minutes the temperature was increasing drastically until it reached around 50°C. Monomer mixed with filler using magnetic stirrer is the only case that reached 70°C in 40 minutes and after that the Sonicator was turned OFF. The range of process time for mixing in this study was in a safe range of device's maximum temperature, which according to its data sheet has a maximum limit of 70°C. After conducting several tests and analyzing the data, the parameters for sonication were set, that is; the process of sonication for the mixing of component A and filler was set 15-minutes and which was then followed by mixing with component B (hardener) for 1-minute setting pulsing time 30-seconds ON and 10-seconds OFF in each case, the amplitude was set at 40% and water was used as coolant.



Figure 2.1. Initial test and trial graph

## 2.2.4 Sample Preparation

### 2.2.4.1 Molds

The molds were cut in a dog bone shape having dimensions according to ASTM D-638.

#### 2.2.4.2 Sample

The samples were prepared according to the mass balance discussed in section 2.2.8. After pouring the liquid mixture in the molds, it was then left for 24 hours to polymerize.

#### 2.2.4.3 Oven

The heating oven shown in figure 2.2 was used for further curing of the samples at 70°C for a total time span of 4 hours.



Figure 2.2 Oven

## 2.2.5 Field Emission Scanning Electronic Microscope (FE-SEM)

A FE-SEM is a microscope that works with electrons instead of light. These negatively charged particles are liberated by a field emission source. The object is scanned by electrons according to

a zig-zag pattern. It is more powerful version of a scanning electron microscope. The scanning electron microscopy is a versatile, non-destructive technique that reveals detailed information about the morphology and the composition of natural and manufactured materials.

#### 2.2.5.1 Technical Specifications

<ul> <li>Sample dimension</li> </ul>	$1 \text{ cm}^2$
<ul> <li>Magnification</li> </ul>	12-900,000x
<ul> <li>Nominal resolution</li> </ul>	1.5 nm at 10 kV and WD=2 mm
• Working distance	1-50 mm
• Probe current	4 pA - 10 nA
<ul> <li>Acceleration voltage</li> </ul>	0.1-30 kV

#### 2.2.6 MTS Q-test-10 Mechanical Tester

The sample mechanical testing was performed according to ASTM D-638-4 standard (Anon 2019). The Q-Test-10 Mechanical Tester was used for mechanical testing of the specimen. It is a very versatile machine which can be used to investigate the mechanical properties of a wide range of materials ranging from metals to composites to plastics. The machine has a load capacity of 10kN. To hold the specimen the machine is supplied with multiple jaws. The machine is supplied with strain gauges and automatic control system. The lower jaw is fixed while the upper jaw is movable and pulls the specimen upwards during testing. The sample is stretched until it breaks. The machine operates at a constant strain rate of 5 mm/min. The testing parameter are set through the graphical user interface of machine operating software. Computer attached to machine shows the load and elongation graph. Before testing transverse speed and measuring loads of the specimen are set. The values were set at 10kN load cell and extension rate of 5 mm/min. The size of the test specimen were provided to the software as per ASTM D-638 standards. The scale of load and extension were reset before each test. Load, Peak Stress, Extension, and Young's Modulus values were determined by operating software. Stress and Strain at each interval were then calculated in Microsoft excel. Five samples of each composition were tested and the results obtained were compared with blank epoxy.

S.No.	Specimen Type	<b>Component A</b>	<b>Component B</b>	Nano filler
		(g)	(g)	(g)
1	Blank Epoxy	20.00	10.00	Nil
2	0.5 wt.% Filler	19.90	9.95	0.15
3	1.0 wt.% Filler	19.80	9.90	0.30
4	2.0 wt.% Filler	19.60	9.80	0.60

#### 2.2.7 Mass Balance

#### 2.2.8 Procedure

First of all tare the weighing balance before placing a beaker and tare it again. After that put the component A in the plastic beaker according to the mass balance, tare the weighing balance again and put the filler, mix the mixture mechanically for a minute and then subject it to sonication process for 15 minutes. After sonication is completed, weight the component B (to avoid trapping of moisture content and foreign particles, the component B is weighted later) according to the mass balance and add it to the above mixture. This is mixed for a minute using sonicator and the final mixture is then poured into the molds. The specimen is to be cured in two steps; 24 hours in ambient conditions and then in the oven for further curing for 4 hours at 70°C. After curing they are removed from the molds and are ready for mechanical testing.

#### **3** Results and Discussion

#### **3.1 Preparation of Biochar**

In this study olive feedstock is used for the preparation of BC. The feedstock was cut into appropriate pieces. Each time before putting the feedstock in the Carbolite tube furnace for pyrolysis the raw material was weighted. After that it was put in a barrel of the pyrolysis unit that was sealed in order to avoid the entrance of air. Since the pyrolysis was carried out in the presence of nitrogen therefore at one end of the tube the supply line was connected to ensure the continuous supply of N<sub>2</sub>. To allow volatiles to escape during the pyrolysis process, a pipe was inserted at the other end of the tube. In this study BC was obtained at four pyrolysis temperatures ( $400 \pm 50^{\circ}$ C,  $600 \pm 5^{\circ}$ C,  $800 \pm 5^{\circ}$ C, and  $1000 \pm 5^{\circ}$ C) and three heating rates ( $5^{\circ}$ C/min,  $15^{\circ}$ C/min,  $50^{\circ}$ C/min). Once the desired temperature was obtained the tube was kept at the same temperature for half an hour and then cooled it down in the presence of N<sub>2</sub> to ambient temperature. At the end of the pyrolysis process the N<sub>2</sub> supply was stopped, the furnace was turned OFF, and the BC was allowed in the same tube to cool overnight. The BC obtained was weighted again followed by grinding and passing through 100µm sieve. After that BC was stored in sealed bottles for further use.

#### **3.2** Composite Preparation

- Cut the mold in dog bone shape according to ASTM D638-4 standard.
- Clean the weighing balance and place a paper on the load cell of the balance.
- Tare the weighing balance before and after every measurement.
- Pour Component-A (low viscosity epoxy resin LPL Cores) in the beaker according to the mass balance.
- Put the predetermined amount of BC powder in the same beaker according to the mass balance.
- Mechanically mix the mixture of Component-A and BC powder for a minute and then for further mixing use sonicator as discussed in section 2.23.
- Use water as a coolant during sonication process.
- Weigh the epoxy resin (Component-B) according to mass balance and mix it with the above mixture of component A and filler (this has to be mixed for a minute using sonicator).

- Care should be taken to avoid mixing of foreign particles during mixing of epoxy resin and fillers.
- Pour the mixture into the molds.
- Remove the air bubbles from the epoxy/filler mixture-if any.
- Keep mixture in the molds for a day in ambient conditions.
- Put the sample in oven at 70°C for 4 hours for curing.
- Remove the samples from the molds.

#### **3.3 Mechanical Properties**

The samples were made in dog bone shape according to ASTM D638 standard. The sample were precisely aligned in the center of the jaws in such a way to avoid kinks and bending. To avoid slippage during the test the jaws were tightened to firmly hold the specimen. Sometimes while fixing the specimen between the jaws it is preloaded. With the help of user interface the values were tared to avoid the consideration of premature load in the test results.

Size	Type I	Type II	Type III	Type IV	Type \
Full length,Is	165	185	165	115	
Parallel lengthJ <sub>2</sub>	67	67	57	83	63.5
Gauge length,I,	50	50	50	25	*
Parallel section width,strong	13	.6	19 (	6	7.62
Thickness,h	7 mm or less ( Recommend 3.2±0.4 mm )		7mm to 14mm	4mm o	r less
Grip section width,strong2	19	19	29	199	9.53
Distance between grips	115	135	115	65	25.4



Figure 3.1 ASTM D638 Specimen Dimensions (Anon 2019)

All the samples were subjected to tensile test on Q-Test-10 tensile tester by pulling out uniformly at a strain rate of 5mm/min. For every specimen the load-elongation curves were recorded. Stress, strain, Young's modulus, toughness, ultimate tensile strength, and percent elongation were calculated from the raw data of load-elongation test.

A typical stress strain cure with different points related to materials properties labelled on it is shown in figure 3.2.



Figure 3.2 Stress-Strain Curve

#### 3.3.1 Stress

When a material is subjected to an external force (F), a resisting force is set up within the material. This internal resistance (force) per unit area acting on a material or the intensity of forces distributed over a given section is called stress.

$$\sigma = \frac{F}{A}$$

 $\sigma$  is the stress expressed in N/m<sup>2</sup>. The unit of stress is Pascal (Pa). Since pascal is a small quantity in practice, we use multiple of this unit i.e. kilo Pascal (kPa), Mega Pascal (MPa), and Giga Pascal (GPa).

#### 3.3.2 Strain

It is the ratio of change in length to the original length.

$$\varepsilon = \frac{\Delta L}{L}$$

It is a dimensionless quantity since it is the ratio between similar quantities.

#### 3.3.3 Yield Strength

Yield strength describes the stress-strain relationship of a material. It is used to describe elastic behavior of the material. Below the elastic behavior limit, stresses or strains applied when relaxed will cause no permanent deformation in the metal. At stresses above the yield strength, the material starts to deform plastically, that is, it does not return to its initial dimensions once unloaded. For applications where plastic deformation is not acceptable, the yield strength is used as the design limit. The yield point of some ductile materials is defined by using the rule of 0.2% offset strain. It has the same units as that of stress.

#### **3.3.4 Young's Modulus**

It is the slope of the stress strain curve in the linear region. At low strain it is also known as modulus of elasticity or elastic modulus which depicts the stiffness of the material. The unit of the Young's modulus is that of the stress.

$$Y = \frac{\sigma}{\varepsilon}$$

#### **3.3.5 Ultimate Tensile Strength (UTS)**

It is the maximum stress material can withstand before breaking. It is the highest point on the stress strain cure. The ultimate tensile strength of a material is calculated by dividing the cross-section area of the material tested by the stress placed on the material. For brittle solids such as ceramics, glasses, and brittle polymers, it is the same as the failure strength in tension. Whereas for deformable materials, it occurs at the onset of necking at strains preceding breakage. UTS is measured in units of force per unit area.

#### 3.3.6 Toughness

It is the ability of the material to absorb energy before fracture in any potentially ductile material and is achieved by distributing energy absorption over the largest possible volume of material. It is also defined as the amount of energy absorb by a material per unit volume until it fractures. It is represented by the area under the stress-strain curve and the strain axis.

$$Toughness = \frac{Energy}{Volume} = \int_0^{\varepsilon_f} \sigma d\varepsilon$$

Where;

 $\epsilon$  is strain  $\sigma$  is the stress and  $\epsilon$  is the strain upon failure. The unit of toughness is J/m<sup>3</sup>.

#### **3.4 Experimental Findings and Observations**

To study the mechanical behavior of neat epoxy and composites, five samples were prepared for each batch. The samples were subjected to tensile test on a Q-test-10 tensile tester with load cell of 10kN and strain rate of 1 mm/min. The data obtained from the tensile test was then used in OriginPro to plot stress-strain curves.

The stress-strain cures of neat epoxy and epoxy added with BC are plotted in figure 3.1a, figure 3.1b, figure 3.1c, figure 3.1d. From the plots it is evident that the sample of neat epoxy has a ductile failure. It is observed that adding lower amount of filler has affected the ductility and the composite has shown a brittle failure, however by increasing the filler amount the composite ductility improved. As far as the ductile behavior of the neat epoxy is concerned, according to the literature the ductility of the neat epoxy is a function of several factors that are; the state of stress, strain, strain rate, temperature, and environment.(Fiedler, Thomas, and Schulte 2005)



Figure 3.3a Stress-Strain Curves (BC400)



Figure 3.3b Stress-Strain Curves (BC600)



Figure 3.3c Stress-Strain Curves (BC800)



Figure 3.3d Stress-Strain Curves (BC1000)

#### 3.4.1 Ultimate Tensile Strength (UTS)

Adding filler to the epoxy matrix has generally enhanced the UTS of the specimen figure 3.4, the numerical values of which are listed below in the appendix in table A. This effect is highest in the specimen prepared with the addition of BC obtained at low heating rate ( $5^{\circ}C/min$ ) and high heating rate ( $50^{\circ}C/min$ ). It is also noted that the specimen prepared from the BC600 has shown remarkable improvement in UTS.

Reinforcing material (fillers) embedded in the matrix of composite form a discontinuous layer or dispersed phase of the composite material. It transfers the applied load to the matrix and also hinders the movement of cracks as a result the specimen can withstand maximum stress and show an improvement in UTS.



Figure 3.4 Ultimate Tensile Strength (MPa)

The better interaction between the filler and the resin enhances the strength of the specimen. The lower amount of filler deteriorated the ductility however the UTS is generally improved by adding BC. In the figure it can be seen that the heating rate has also influenced the UTS in each batch. The maximum pyrolysis also affects the UTS and this is evident in the batch obtained by adding higher amount of fillers.

#### 3.4.2 Young's Modulus

The values of the Young's modulus of neat epoxy and epoxy added with BC obtained at different heating rates and maximum temperature are in appendix in table B.



Figure 3.5 Modulus of Elasticity (MPa)

It observed that the elastic modulus gets deteriorated with the increase in filler percentage. It is also seen that for the specimen made of BC600, Young's modulus is slightly improved in all of the three cases of filler percentages figure 3.5. Furthermore, the effect of heating rate is obvious in specimen prepared with BC obtained at 15°C/min. Increasing the amount of filler further affected the elastic modulus of specimen. It is observed that the addition of 0.5wt.% filler is more favorable to enhance the Young's modulus of the composite as compared to 1wt.% and 2wt.% of fillers.

#### 3.4.3 Toughness

The values of the toughness of neat epoxy and epoxy added with BC are given in appendix in table C.



Figure 3.6 Toughness (MJ/m<sup>3</sup>)

It is seen that the toughness of the specimen has increased by increasing the amount of filler. The maximum pyrolysis temperature as well as the heating rate has shown slight improvement in the toughness only in 0.5wt% of filler. Whereas in other two cases of filler percentages it is affecting the toughness. However, the increasing trend in toughness is noticed by adding more fillers to the resin.

#### **3.4.4 Elongation at Fracture**

The elongation of the neat epoxy and epoxy added with BC are given in appendix in the table D.



Figure 3.7 %Elongation

The lower amount of filler addition has affected the elongation negatively except for the heating rate of 15°C/min. However, by increasing the amount of filler, the elongation of composites has improved. The improvement in elongation is quite evident in batch of 2wt.% of filler. The effect of heating rate is more significant as compared to the maximum pyrolysis temperature of BC fillers.

#### 3.5 Field Emission Scanning Electron Microscope (FE-SEM) Analysis

Morphology of olive bio-char (BC) was investigated by Field Emission Scanning Electron Microscope (FE-SEM-ZEISS SUPRA-40TM). Below in figure 3.6 are the four images of BC obtained at 400°C, 600°C, 800°C, and 1000°C with heating rate of 15°C/min.



Figure 3.8 FE-SEM-Image

As the pyrolysis gets start the volatile matters are removed which leave behind a porous structure. Besides pores the FESEM images in figure 3.7 also show structure of the channels. In both sets of images it can be seen that the size of the pores as well as the length of the channels develop as the pyrolysis temperature increases. BC400

BC600

![](_page_30_Figure_2.jpeg)

BC800

BC1000

Figure 3.9 FE-SEM-Image

The FE-SEM analysis of bio-char also reveals that it has a heterogeneous pores and a rough texture.

## 4. Conclusion

BC obtained from olive tree and pyrolyzed at different temperatures and heating rates was used as filler to prepare the polymer composites based on epoxy resin. Five temperature ranges, three heating rates, and three different percentages of BC were used in the preparing polymer composite and to study their mechanical properties. In general, it is observed that adding the carbon fillers has increased the load bearing capacity of the epoxy matrix. It is also observed that adding lower percentage of carbon fillers negatively affected the ductility of the matrix, while, increasing the filler percentage led to improvement in ductile behavior of the epoxy matrix.

The best results were achieved by 0.5 wt.% and 1 wt.% regarding UTS. The heating rate has also influenced the UTS in each batch. Among all the batches obtained at different filler percentages, BC600 showed increase in UTS.

The elastic modulus gets deteriorated by increasing filler percentage. It is noticed that for the specimen made of BC600 it is slightly improved in all the three cases of filler percentages. Furthermore, the effect of heating rate is obvious in specimen prepared with BC obtained at 15°C/min. Increasing the amount of filler affected the elastic modulus of specimen. It is observed that the addition of 0.5wt.% filler is more favorable to enhance the young modulus of the composite as compared to 1wt.% and 2wt.% of fillers.

Toughness of the polymer composites increases by increasing the percentage of BC. The maximum toughness was reached by the specimen prepared using 2wt.% of filler. It is worth mentioning that the composites behavior transformed from brittle at lower filler percentage to ductile at higher filler percentage. The pyrolysis temperature as well as the heating rate has shown slight improvement in the toughness only in the batch of 0.5wt.% of filler.

The lower amount of filler addition has affected the elongation negatively except for the heating rate of 15°C/min. However, by increasing the amount of filler addition, the elongation of composites improved. The improvement in elongation is higher in the batch of specimen prepared from 2wt.% filler.

In order to further investigate the effect of BC on mechanical properties of polymer composites, the trend between UTS and toughness can be noticed. When the UTS is increased the toughness is decreased and vice versa. 0.5wt.% and 1wt.% filler addition prove to be the best choice for

improving elastic properties, whereas higher percentages of the filler addition reduce the beneficial effect of filler in regard to the UTS and young modulus. For the improvement of toughness and elongation 2wt.% proves to be the best choice.

Finally, it is plausible to say that BC effects behavior of the composites. The higher amount of filler addition to the epoxy matrix transforms it from brittle to ductile. We can tune the properties of the composites by changing filler percentages, the heating rates and pyrolysis temperature.

# 5. Appendix

## Table A

Ultimate Tensile Strength (MPa)

Neat Epoxy	y 17±1	.4		
0.5wt%	400°C	600°C	800°C	1000°C
HR				
5°C/min	20.8±3.2	24.3±1.8	22.2±1.1	23.3±0.9
15°C/min	13.7±1.1	23.1±0.9	16.5±0.9	18.5±1.9
50°C/min	20.9±1.7	26.8±1.1	23.3±1.0	21.4±3.0
1wt%				
HR				
5°C/min	18.7±1.7	21.1±2.3	16.3±2.9	22.9±0.2
15°C/min	15.8±1.0	22.5±0.7	15.3±2.1	11.2±0.3
50°C/min	17.0±0.5	18.2±2.1	23.2±1.4	17.0±2.4
2wt%				
HR				
5°C/min	18.0±0.8	23.2±1.4	18.0±0.9	19.1±1.7
15°C/min	17.4±2.0	28.9±0.8	22.0±0.2	11.7±0.8
50°C/min	28.2±0.6	16.9±0.9	18.9±0.1	17.0±0.6

## Table B

## Modulus of Elasticity (MPa)

Neat Epoxy	y 1286±18	35		
0.5wt%	400°C	600°C	800°C	1000°C
HR				
5°C/min	1786±179	2103±89	1917±100	1798±30
15°C/min	968±142	1611±60	1187±84	1335±164
50°C/min	1850±133	2144±117	2120±87	1796±258
1 wt%				
HR				
5°C/min	1446±153	1692±221	1476±122	1989±126
15°C/min	1159±81	1780±66	1230±216	771±56
50°C/min	1246±55	1637±152	2130±92	1463±247
2wt%				
HR				
5°C/min	1384±65	1780±161	1399±90	1377±141
15°C/min	1314±124	2011±67	1508±65	756±96
50°C/min	2030±78	1306±66	1524±43	1188±68

## Table C

E

# Toughness (MJ/m<sup>3</sup>)

Neat Epoxy	0.5±0.0	13		
0.5wt%	400°C	600°C	800°C	1000°C
HR				
5°C/min	0.30±0.07	0.37±0.08	0.43±0.12	0.41±0.07
15°C/min	0.58±0.03	0.56±0.05	0.61±0.11	0.67±0.13
50°C/min	0.31±0.04	0.51±0.03	0.49±0.08	0.46±0.04
1 wt%				
HR				
5°C/min	0.49±0.05	0.66±0.10	0.26±0.08	0.40±0.13
15°C/min	0.74±0.18	0.41±0.04	0.51±0.09	0.62±0.03
50°C/min	0.76±0.08	0.43±0.09	0.43±0.08	0.54±0.05
2wt%				
HR				
5°C/min	0.72±0.07	0.73±0.10	0.61±0.07	0.59±0.17
15°C/min	0.72±0.07	0.78±0.05	0.78±0.05	0.60±0.06
50°C/min	0.55±0.08	0.56±0.06	0.69±0.03	0.80±0.06

## Table D

# %Elongation at Fracture

Neat Epoxy	4.08±0.0	08		
0.5wt%	400°C	600°C	800°C	1000°C
HR				
5°C/min	2.9±0.3	2.2±0.3	2.7±1.1	2.4±0.3
15°C/min	5.3±0.4	3.4±0.3	4.6±0.6	4.6±0.5
50°C/min	2.2±0.2	2.7±0.2	2.8±0.4	3.0±0.3
1wt%				
HR				
5°C/min	3.7±0.6	4.0±0.1	2.1±0.4	2.8±0.2
15°C/min	5.3±1.0	2.6±0.1	4.7±0.7	6.7±0.3
50°C/min	5.6±0.4	3.1±0.4	2.5±0.3	4.2±0.4
2wt%				
HR				
5°C/min	4.8±0.3	4.3±0.5	4.4±0.9	4.0±0.7
15°C/min	5.2±0.4	3.7±0.2	4.6±0.2	6.2±0.5
50°C/min	3.0±0.3	4.3±0.2	4.7±0.2	5.9±0.3

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