



Preparing Expandable Graphite from Biomass waste and its Application as Fire-Retardant Agent in Epoxy Resin

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Abstract

Expandable Graphite (EG) is functional filler for resins. Synthesized Expandable Graphite (EG) from Biomass agriculture waste (**rice husk**) by graphitizing carbonized this waste undergoing severe oxidation conditions and then it is saturated with fire retardant agents like sodium borates and phosphoric acid. This paper describes the chemical properties of natural graphite and Expandable Graphite (EG) which is developed to be easily integrated and effectively dispersed into epoxy resin. Fire tests were carried out using wood specimens painted with polymers where specimens showed far extent in fire retarding. The addition of expandable graphite flake was found to increase the flame retardant effectiveness of epoxy resin systems. The use of graphite improved the physical characteristics of the char by increasing the amount of the insulating layer and reducing crack formation. The developed intumescent resin using expandable graphite as an additive showed markedly improved results for time to ignition, heat absorbed, mass loss, and flame spread. The smoke from burned resin/graphite system was reduced compared to that obtained from the intumescent resin alone

Keywords: Food waste, Biomass agriculture waste (rice husk), Expandable Graphite, Epoxy Resin, Fire Retardant agent.

1- Introduction

As fire safety has always been a major concern, fire protection is in high demand. One of the key approaches to improving fire protection entails adding flame retardants to polymeric materials, because most synthetic polymers are easily ignited due to their high content of hydrocarbons, which is excellent fuels for fires. Currently, efficient flame retardancy is achieved through specific solutions tailored to different kinds of polymeric materials, as they have different properties [1–3]. Flame retardancy is specific with respect to the flame retardant mechanisms and flame retardant's reactions with polymeric materials [4–7] and with other ingredients, such as additional flame retardants, fillers/fibers, additives, adjuvants, and synergists [8]. Flame retardancy is specific with respect to the protection goal and fire scenario; ignition scenarios require different approaches from developing fires or fully developed fires [9]. Different flame retardants are even favored for the same polymer depending on whether it is applied in bulk, as a composite, or in the form of fibers or foam. Thus, a multitude of different flame retardants in various combinations are used to protect the entire spectrum of foam-containing consumer goods [10]. Generalized approaches of

efficient combinations working in different matrices, such as flame retardants containing Br combined with Sb_2O_3 or ammonium polyphosphate (APP) with pentaerythritol (PER), are rare; furthermore, environmental concerns mean that halogen-free systems are preferred. One of the champions among the currently proposed flame retardants that have found application in today's products is the synergistic combination of expandable graphite (EG). This approach has become legendary for the excellent flame retardancy it provides to epoxy resins [11–14]. In this feature article, we turn the scientific spotlight on the concept, mechanisms, and role of the synergistic EG in epoxy resins in order to evoke the applause this approach deserves [15].

This work deals to prepare an expandable graphite from biomass agriculture waste (rice husk), and evaluate its application for fire retardant to epoxy resin.

Materials and Method

Epi-chloro hydrine (ECH), Phenylene diamine, Diglycidyl ether of bisphenol-A (DGEBA), sodium hydroxide, concentrated sulphoric acid, potassium permanganates, sodium borates, ferric chloride, and hydrochloric acid. All chemicals were supplied by

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Receive Date: 03 April 2023, Revise Date: 17 May 2023, Accept Date: 14 June 2023

DOI: [10.21608/EJCHEM.2023.203892.7818](https://doi.org/10.21608/EJCHEM.2023.203892.7818)

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Sigma Aldrich Co. with purity 99, 9% and directly used, biomass agriculture waste (**rice husk**) from surrounding environment.

Preparation of epoxy resin [16]

Under nitrogen atmosphere, 1mol of each (DGEBA) and ECH were mixed in 500 mL four-necked flask at 50°C, after (DGEBA) was dissolved; the mixture solution was stirred continuously. The temperature was raised to 70°C and kept for 3 h. Then the solution was cooled down to 50°C, sodium hydroxide solution was added drop wise into the flask and the temperature was kept at 50°C continuously for another 3 h. After recovering the solvent, the produced salt during the reaction was filtered off and the filtrate was washed with excessive water, then with the volatiles evaporated (including solvent and water) under reduced pressure, the flexible epoxy resin was obtained as a light yellow liquid product, then the epoxy resin was mixed uniformly with curing agent (Phenylene diamine) in a certain proportion. The mixture removed bubbles in a vacuum oven, poured into a Teflon mold, then cured at temperature 70°C for a period of time.

Preparation of graphite from Biomass agriculture wastes (rice husk) [17]

Biomass agriculture wastes (**rice husk**) were washed several times with water mixed with liquid detergent, to remove any unwanted components. The washed Biomass agriculture wastes (**rice husk**) were laid out on galvanized iron sheets and sun-dried for 3 days. Biomass agriculture wastes (**rice husk**) were further conditioned in a laboratory oven at 105 °C for 24 h before being cut into ~10 mm long pieces and milled in an analytical mill for 10 min. The resulting agriculture waste powder was sieved (mesh 100) before carbonization. The carbonization and graphitization of biomass agriculture waste (**rice husk**) was performed by the following method. Briefly, 5 g of biomass agriculture waste (**rice husk**) was placed and covered in a crucible with limited air access. Covered crucibles containing biomass agriculture waste (rice husk) were transferred into a muffle for carbonization at 400 °C for 5 h. The carbonized material was ground into a powder and sieved (mesh 100) before graphitization. The carbonized material and FeCl₃.6H₂O (at 2:1 carbon-catalyst mass ratio) were added to distilled water (100 mL). The pH of the solution was adjusted ~2 by

adding HCl. The mixture was heated at 60 °C for 5 h, using a hot plate, while being continuously homogenized at 1000 rpm by a high-speed homogenizer equipped with a dispersing element. Graphite was separated from the homogenized solution by vacuum filtration and dried in a laboratory oven at 105 °C for at least 48 h before further use.

Preparation of expandable graphite [18]

Reactants were weighed with mass ratio of C₄: KMnO₄: H₂SO₄ (98%): Na₂B₄O₇• 10H₂O (1.0:0.4:5.5:0.6), mixed in a 250 mL beaker and stirred at a controlled temperature using a water bath. After maintaining for 40 min, the solid phase was washed with de-ionized water until the pH of the waste water reached 6.0–7.0. The solid product was dipped in water for 2 h, then filtrated and dried at 60–70°C for 6 h, EG was obtained.

Detection of initiation expansion temperature:

0.3 g of the prepared EG is spread on evaporating dish, then the dish is placed in oven (when the controlled temperature is lower than 300 °C), which has been set as a constant temperature. After a definite time, take the sample out and measure its volume with a 5.0 mL graduated flask. In experiment, the temperature corresponding to 1.5 times of EGs' initiation volume is defined as EGs' initiation expansion temperature which was 300°C.

Detection of expansion volume (rate):

EV is an important factor to judge of the anti-flame properties and defined as the volume of expanded graphite corresponding to 1.0 g of expandable graphite, written as mL/g. three EG samples with the mass of 0.3 g are prepared, and they are heated at 100 °C, 200 °C, 300 °C, respectively, then the volume is detected by mL graduated flask, and the higher the expansion temperature is, the shorter expansion time is selected, which was 460 mL g⁻¹.

Physical Measurements [19]

Fourier transform infrared (FTIR) spectrum of the epoxy resin, natural graphite and expandable graphite were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{\max} in cm⁻¹) on KBr disks. X-ray diffraction (XRD) was recorded on Xpertpro-Panalytical X-ray diffractometer, also HNMR spectrum was recorded on Varian Gemini 200 MHz spectrophotometer, limiting oxy-index test was proceeded on limiting oxy-index tester model ASIAN

F701 and ignitability test was preceded on single flame source tester model manual/front (HDB/VD). TGA test was preceded on Perkin analyzer (TGA-8000), Micrographs of SEM were obtained using (QUANTA 250 SEG, HOLANDA) micro analyzer microscope. The samples were prepared by deposition of a thin gold film, sputtered using a Balzers S150A deposition system. Elemental analysis for expandable graphite and epoxy resin is proceeded using "PerkinElmer 2400 CHNS Organic Elemental Analyzer" this instrument calculates the percentages of elemental concentrations.

Results and discussion:

FTIR and HNMR of epoxy resin after curing:

The structure of the prepared RESIN was established by studying their IR and HNMR spectra. The IR spectra of prepared polymer (Fig.2,3) shows bands at $(3450-3400\text{ cm}^{-1})$ (γ OH), $(2920-2900\text{ cm}^{-1})$ (γ CH₂) and $(1720-1700\text{ cm}^{-1})$ (γ C=O), **(693-800)** (γ N-H). The HNMR spectra of the polymer showed bands at (σ 6.2-8) due to aromatic protons and ($-\text{CH}=\text{CH}-$), at (σ 4.2) due to ($-\text{CH}_2-\text{C}=\text{O}-$) group, at (σ 1.7) due to two methyl groups of bromo bis phenol -A, at (σ 1.2) due to protons of ($-\text{CH}_2-$) group.

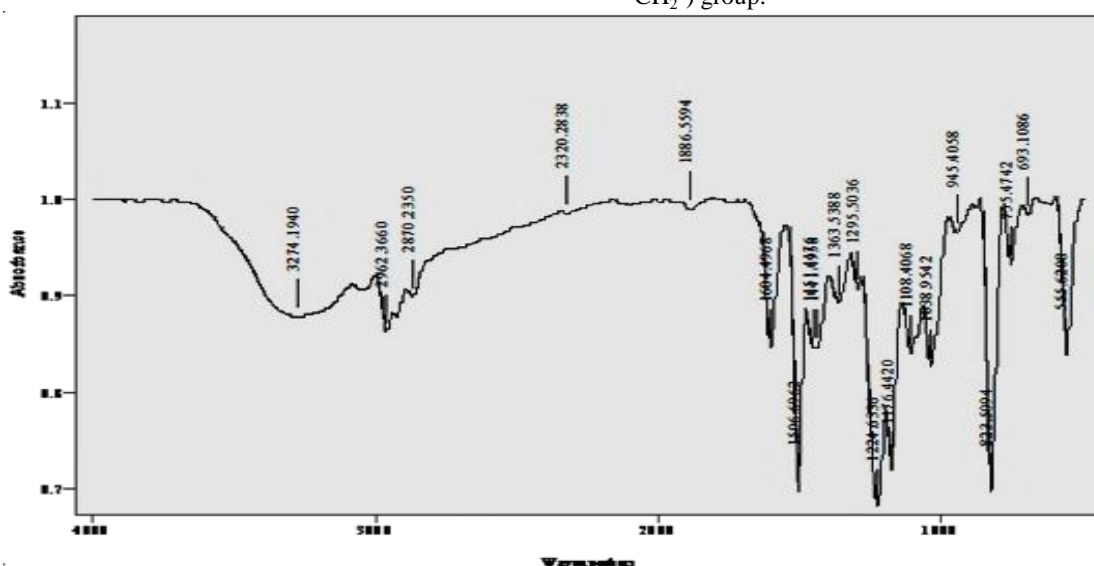


Figure (2) HNMR of prepared polymer.

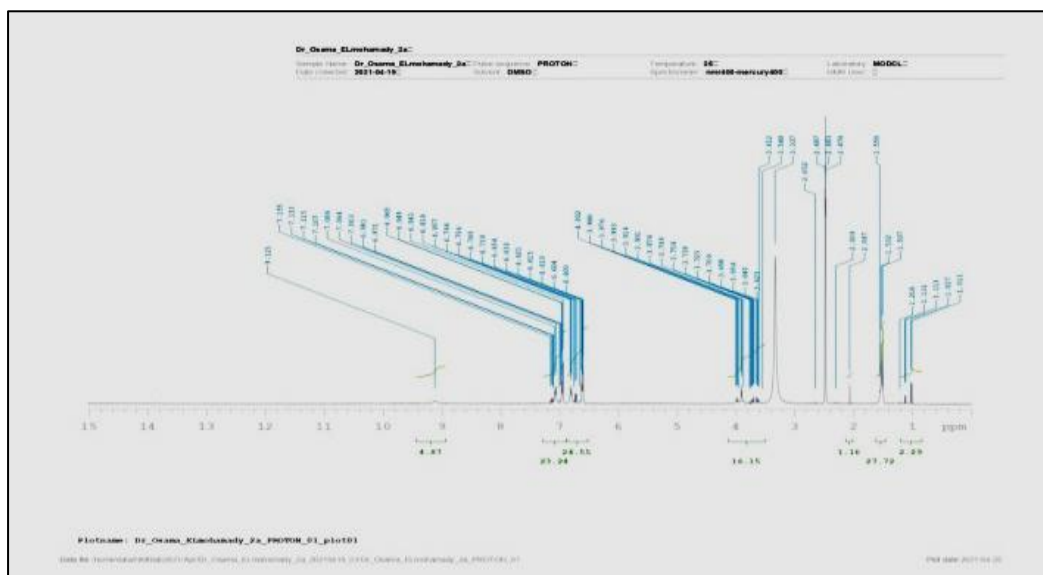
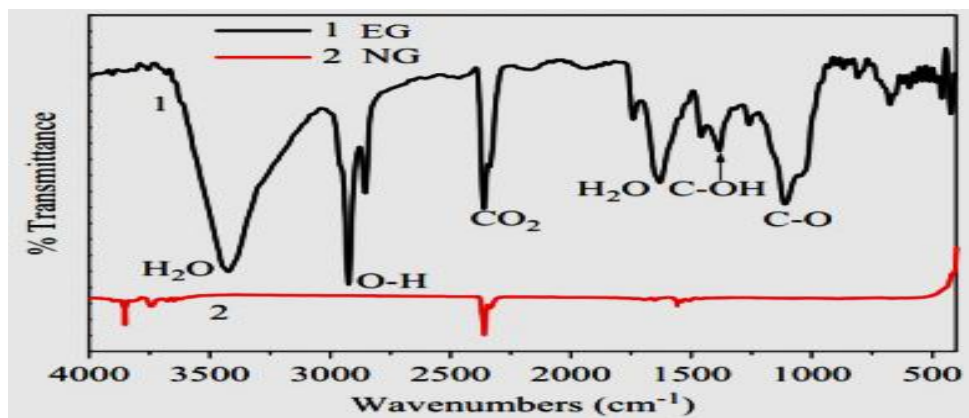


Figure (3) IR of prepared polymer.

FTIR of Natural and Expandable graphite:-

FTIR spectrum of natural and expandable graphite is shown in (Fig. 4). To explore the difference of inner structure between expandable graphite (EG) and natural graphite (NG), FTIR spectra analyses are conducted. It is noted that NG flakes show few absorption bands in the 400–4000 cm^{-1} range of FTIR spectra, as demonstrated in (Fig. 4), but different results are shown on EG. The peak around 1111 cm^{-1} is due to the stretching vibrations of (C=O) groups on the

surface of EX, the absorption peak at 1384 cm^{-1} can be assigned to the bending vibration of COH, and the peaks at 2924 and 2854 cm^{-1} are resulted from O–H stretching vibrations. The broadband around 3440 cm^{-1} and the peak at 1630 cm^{-1} are attributed to the presence of hydroxyl groups as a result of absorbed water, and the peak at 2360 cm^{-1} is caused by CO₂ in the air. The results show that some kinds of groups or atoms are introduced into EG compared with NG [20].

Figure (4) IR of natural and expandable graphite**Elemental analysis:-
Expandable graphite**

Element	Percentage%
Fixed carbon	93%
Ash	6%
Others	1%
Total	100%

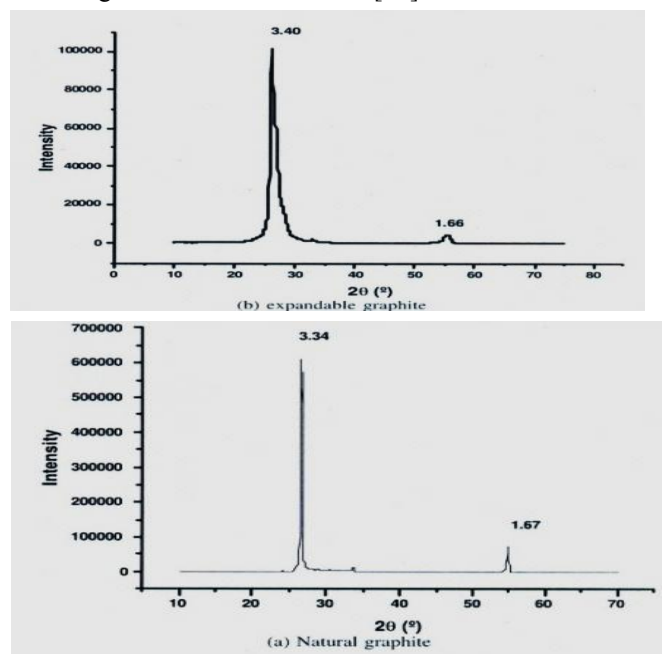
Epoxy resin

Element	Percentage%
Carbon	39.4121 %
Hydrogen	4.0001 %
Nitrogen	5.7637
Others	50.8241 %
Total	100%

XRD of Natural and Expandable graphite:-

The X-ray diffraction (XRD) pattern of EG and EG is displayed in (Fig. 5). XRD analysis results for material graphite and the expandable graphite are shown in (Figure 5). Diffraction peaks of 3.34 and 1.67 Å are the two characteristic spectrums of natural graphite. Because of graphene planes, the peak of 3.34 Å is strengthened during XRD detection. In the XRD analysis of the prepared expandable graphite, the characteristic peak of 3.34 Å is replaced with 3.40 Å. The results show that

the layer space is bigger than the natural graphite and a new substance has inserted into graphene planes which might be Na₂B₄O₇·10H₂O [21].

**Figure (5) XRD pattern of NG and EG
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Receive Date: 03 April 2023, Revise Date: 17 May 2023, Accept Date: 14 June 2023

DOI: [10.21608/EJCHEM.2023.203892.7818](https://doi.org/10.21608/EJCHEM.2023.203892.7818)

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As shown in fig. 6 natural graphites are sheets shaped particles (Fig 6.A) and in expandable graphite expands perpendicular to the plane when a critical temperature is reached (Fig 6.B), after expansion the structure is foam-like because of the increased distance between graphite layers due to oxidative agents and high temperature levels with particles sizes ranges between 200-300 μ m [22].

Thermogravimetric analysis:-

The thermal analysis of the resin with fire retardant show endothermic effects in the temperature ranges 50–200, 350–500, and 650– 730 $^{\circ}$ C (Fig.7).The first effect is responsible for the physicochemical processes associated with the removal of free, physically and chemically bound water; the second marks the beginning of thermal decomposition of the fire retardants; the third shows the melting of the eutectic, thermal decomposition of hydrocarbons, and residual removal of gas inclusions [23].

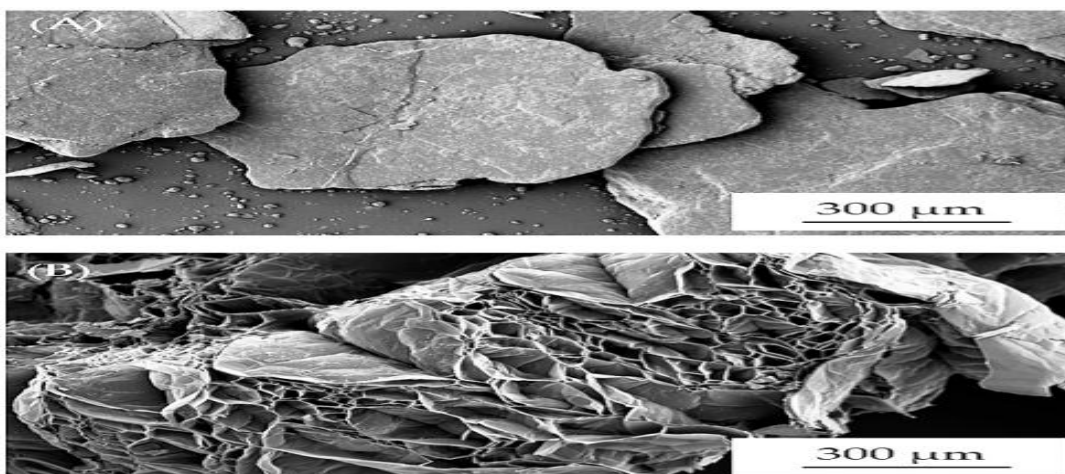


Figure (6) SEM of graphite (A) before (B) after expansion.

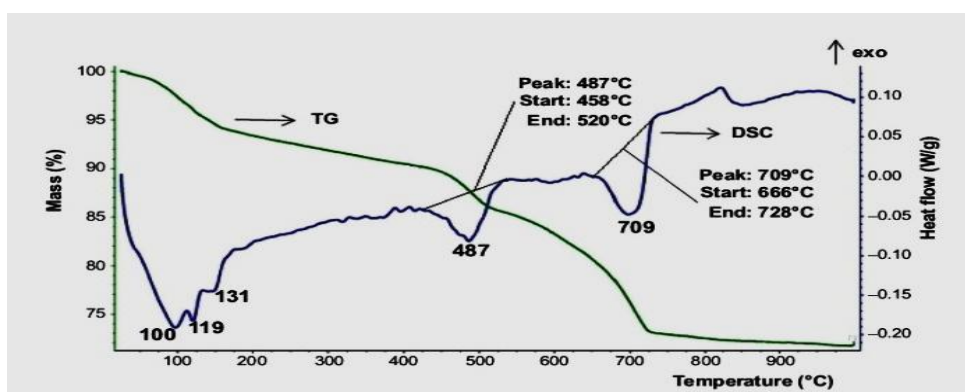


Figure (7) thermogravimetric curves of resin

Table (1)

Sample	Limiting oxygen index
Sample (1)	21%
Sample (2)	25%

Table 2

Sample	MV transduce out	Heat flux applied	Temperature	Observation and Time to ignition
(Sample 1)	Mv 1.6	Kw/m ² 10	°C 433	flammable after 1 Min
(Sample 2)	Mv 1.6	Kw/m ² 10	°C 433	Not flammable after 5 Min
	Mv 2.5	Kw/m ² 15	°C 505	Not flammable after 5 Min
	Mv 2.8	Kw/m ² 20	°C 534	Not flammable after 5 Min
	Mv 4.3	Kw/m ² 25	°C 623	Not flammable after 5 Min
	Mv 5	Kw/m ² 30	°C 657	Not flammable after 5 Min
	Mv 6	Kw/m ² 35	°C 700	Not flammable after 5 Min

Limiting oxygen index:

In this test two specimen of wood the first was uncoated absolutely (sample 1); the second was coated with (polymer/EG) system (examined sample 2 which containing about 15%wt Expandable graphite) with dimension of (80 mm long by 10 mm wide by 4 mm thick). Limiting oxygen index test shows increase in the amount of oxygen required to ignition process in the sample with EG due to presence of fire retardant agents between layers of EG as shown in table (1). [24]

Ignitability test: -

In this test two specimen of wood the first was uncoated absolutely (sample 1); the second was coated with (polymer/EG) system (sample 2 which containing about 15%wt Expandable graphite) with dimension of (25 cm x 25 cm x 2.5 cm). Ignitability test was used to evaluate the fire retardancy of samples, the following (table 2) shows the time of burning of coated wood specimens. It is clear that the time of burning specimen is greater than that of uncoated plywood specimen. It is attributed to the presence of added particles in resin chain acting as fire retardant which take long time to burn. [25].

CONCLUSIONS:

The addition of expandable graphite flake was found to increase the flame retardant effectiveness of epoxy resin systems. The use of graphite improved the physical characteristics of the char by increasing the amount of the insulating layer and reducing crack formation. The developed intumescent resin using expandable graphite as an additive showed markedly improved results for time to ignition, heat absorbed, mass loss, and flame spread. The smoke from burned resin/graphite system was reduced compared to that obtained from the intumescent resin alone. In

ignitability test treated sample needed up to 700C and more than 5 min to be burned, also in limiting oxy-index treated sample needed about 25% oxygen to be burned and showed good thermal stability in thermal degradation test.

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