

## Synthesis, Characterization of Some Fire-Retardant Polymers and their Application

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### Abstract

Food waste or vehicle rubber tyres were used to make activated carbon and carbon nanotubes. Activated carbon was made by two different activation methods: first, phosphoric acid and later potassium hydroxide. These particles were developed that could be easily integrated and effectively dispersed into polymers. Fire tests like ignitability, limiting oxy-index, and thermal stability were carried out using wood specimens painted with polymers where specimens showed far extent in fire retarding.

**Keywords:** Food waste, Activated carbon, Carbon nanotubes, Fires.

### 1. Introduction

Fire triangle (fuel, oxygen and heat) or ignition triangle is a simple model for understanding the necessary ingredients for most fires [1]. The triangle has the three elements necessary to initiate fire if they are present and combined in the right mixture [2]. Fire can be prevented or extinguished by removing any one of the elements in the fire triangle. For example, covering a fire with a blanket removes the "oxygen" part of the triangle and fires can be extinguished. Recently, scientists and experts changed the fire triangle to fire tetrahedron [3]. The fire tetrahedron represents the addition of a component i.e., the chemical chain reaction, to the three already present in the fire triangle. Once a fire has started, the resulting exothermic chain reaction sustains the fire and allows it to continue until or unless at least one of the elements of the fire is blocked. Foam can be used to deny the oxygen it needs. Water can be used to lower temperature of the fuel below the ignition point or to remove or disperse the fuel [4]. Halogen organo- compounds can be used to remove free radicals and create a barrier of inert gas in a direct attack on the chemical reaction responsible for the fire [5]. In addition, ignition can be defined as oxidation reaction in which the ignited material combines with oxygen with reaction velocity reaching to 150 m/sec [6]. Ignition will occur when all required conditions to start a fire occur, producing either a smoldering or a flaming fire. This will often be induced by the addition of heat to a fuel in air, which can be caused by various sources such as exothermic chemical reaction, friction, solar radiation and electricity [7]. The temperature required for ignition to occur varies depending on the fuel. The flash point is the minimum temperature at which fuel vapor is momentarily ignited in air by an external ignition source. However, this will not necessarily cause combustion and produce a fire. The flame or fire point is the minimum temperature at which enough vapor is produced to allow continued combustion. This is usually a few degrees higher than the flash point. Both the flash and flame points are determined by placing a small amount of specimen in an airtight container, gradually increasing its temperature whilst periodically adding an ignition source and then measuring the points at which the flash and flame point is reached [8]. The spontaneous ignition temperature also known as the auto-ignition points is the lowest temperature at which a

substance will ignite without any external ignition source [9]. This is measured by heating a specimen, studying the central temperature of the material and documenting the temperature at which ignition spontaneously occurs. The flash and flame point and spontaneous ignition temperature are the lowest temperatures at which a material has ignited when heated experimentally though these actual temperatures can vary and so should only be used as a guideline. Different fuels also have individual lower and upper flammability, the lowest and highest concentrations of flammable gas required for combustion. If the concentration falls outside of this flammability range, combustion will not generally occur [10].

### 2. Chemicals and methods

Orthophosphoric acid ( $H_3PO_4$  85 wt %), hydrochloric acid (HCL 37%), potassium hydroxide (KOH 99.99%), melamine ( $C_3N_6H_6$  99%), Ferro oxalate ( $Fe_2(C_2O_4)3 \cdot 6H_2O$  99%), lead acetate Pb ( $CH_3COO$ )<sub>2</sub> (99.99%) and methanol ( $CH_3OH$  99.9%).

**Food waste specimen [11]** in this investigation, the stating material was food waste. It was furnace burned for 72 hours at roughly 100 degrees Celsius. It was ground to a particle size of less than 300  $\mu m$ .

#### Activated carbon preparation

The preparation of activated carbon was done through two activation steps as following:

**1st activation step with phosphoric acid [12]** Activated carbon was prepared by adding 11.4 g of carbon produced from food waste as starting material with 11.9 mL 85% phosphoric acid ( $H_3PO_4$ ) and 150 mL of deionized water. The mix was mixed at 100 degrees Celsius for 2 hours before being departed to dry for 24 hours. The dried specimen was then pyrolysed in an oven using at 500 degrees Celsius with a half hour hold time and a heating average of 2 degrees Celsius min<sup>-1</sup>. The pyrolysis was carried out below nitrogen gas atmosphere with a flow average of 100 mL min<sup>-1</sup>. The specimen was then cooled to room temperature before it was washed with water to eliminate any contaminations that may have been obtained through activation and to neutralize the pH to around 6-7. The specimen was dried for 24 hours at 120 degrees Celsius. The specimen was named as PP.

**2nd activation step with potassium hydroxide [13]** The PP specimen was exposed to a second activation step, where 3.12 g of PP was integrated with KOH with a

weight ratio of 1:3.5 and deionized water was added before being mixed at 100 degrees Celsius for 1 hour. The specimen was then dried for 24 hours at 120 degrees Celsius. The dried specimen was then pyrolysed at 500 degrees Celsius, with a half hour hold time at a heating average of 2 degrees Celsius min<sup>-1</sup> below nitrogen gas atmosphere. The specimen was then cooled to room temperature before being washed in the first with HCl to remove any impurities and secondly with deionized water to neutralize the pH. The specimen was dried for 24 hours at 120 degrees Celsius. The specimen was named as PK.

#### Carbon nanotubes preparation [14]

For the making of carbon nanotubes, 1 g of PK specimen was integrated with 17.5 g of melamine and 0.5 g of iron oxalate. It was then mixed for 4 hours in a methanol before being dried at 120 degrees Celsius for 24 hours. The specimen was then pyrolysed at 600 degrees Celsius with a heating average of 2 degrees Celsius min<sup>-1</sup> and held for 3 hours before being pyrolysed to 900 degrees Celsius with a heating average of 2 degrees Celsius min<sup>-1</sup> and held for 1 hour. The specimen was then cooled to room temperature before washing and drying for 24 hours at 80 degrees Celsius. The specimen was named as CNTs.

The prepared fire retardant agents were blended into epoxy resin to proceed thermal and fire tests.

### 3. Results and Discussion

#### - Structure of activated carbon and carbon nanotubes [15]:-

Figure 1 shows X-ray diffraction of the prepared specimens. The diffraction lines that correspond to crystal-like and shapeless cellulose states at 2 of 18 and 22 degrees, respectively, were seen in the food waste specimen. Diffraction lines corresponding to KHSi<sub>2</sub>O<sub>5</sub> at 2

of 28.4°, as well as KCl at 2 of 40.6 and 50.2°, were also seen in the raw material (food waste). There are just two diffraction lines for both the AC (PP and PK) specimens, at 24.9 and 42.9° for the PP and 22.3 and 43.1° for the PK, which are ascribed to crystal-like graphite with slightly varying crystallinities. The CNTs specimen, on the other hand, had more diffraction lines than the ACs specimens, mostly in the form of diffraction lines.

#### SEM-EDX analysis [16]:-

Fig. (2) shows the ACs created by the epoxy resin without any fire retardant additives, as well as the CNTs derived from food waste, at various magnification levels. As shown in Fig. 3a, the PP specimen had a porous or semi-porous carbonaceous structure, but the PK specimen had a better porous structure with more channeling pores and multilayer growth, as shown in Fig. 3b. This is consistent with the SBET data, which revealed an increase in surface area and pore Specimen s volume. The CNTs images in Figure 3c clearly showed carbon nanotubes, which agrees with the SBET result that the expected creation of MWCNTs with the average number CNT has a value of 40. Table 1 shows the EDX results for the food waste, PP, PK, and CNTs. The EDX analysis is a surface method that decides the elemental composition in wt%, with C increasing by 31.6 wt% from the food waste to PP specimen. This might be belongs to the fragmentation of lignin and the formation of porous carbon formations, which causes the analysis of other cellulose components and the generation of phenolic gases. The 2.3 wt% of K in the food waste specimen, on the other hand, was lost due to the creation of activated carbon (PP), as indicated in Table (1). Phosphorus, showed the converse affinity, with a 0.2 wt percent increase between food waste and PP and a 2.2 wt percent increase between food waste and PP

Table (1)

Specimen s		Food waste	PP	PK	CNTs
<b>PPW</b>					
<b>Elemental composition (wt.% on dry basis)</b>	% C	41.94	76.94	69.03	68.35
	% H	5.60	1.88	1.40	0.89
	% N	1.61	0.56	0.30	7.4
	% S	0.3	0.30	--	--
	% O	50.55	20.32	29.57	23.36
<b>EDX analysis (wt.% on dry basis)</b>	C	56.5	88.1	80.2	80.6
	O	40.3	9.80	19.80	15.3
	Si	-----	-----	-----	-----
	P	0.21	2.22	-----	-----
	Fe	-----	-----	-----	4.01
	K	2.31	-----	-----	-----

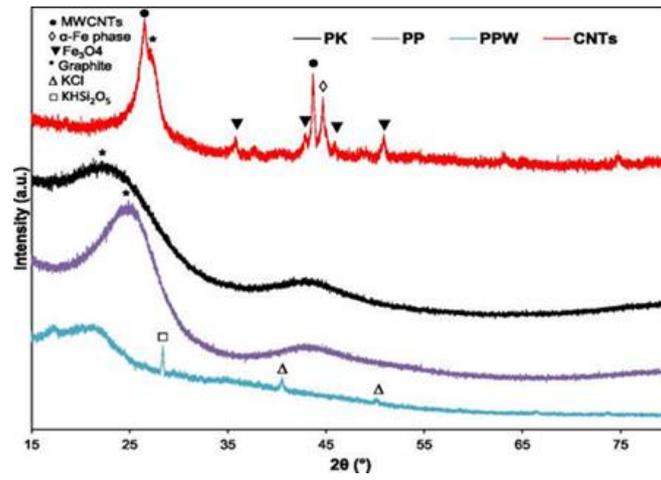


Fig. (1) X-ray diffraction patterns of specimens.

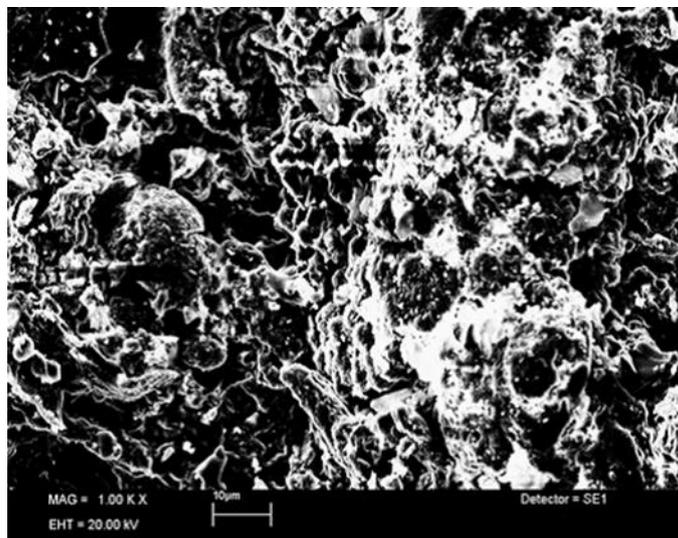


Fig. 2 SEM micrograph of epoxy resin

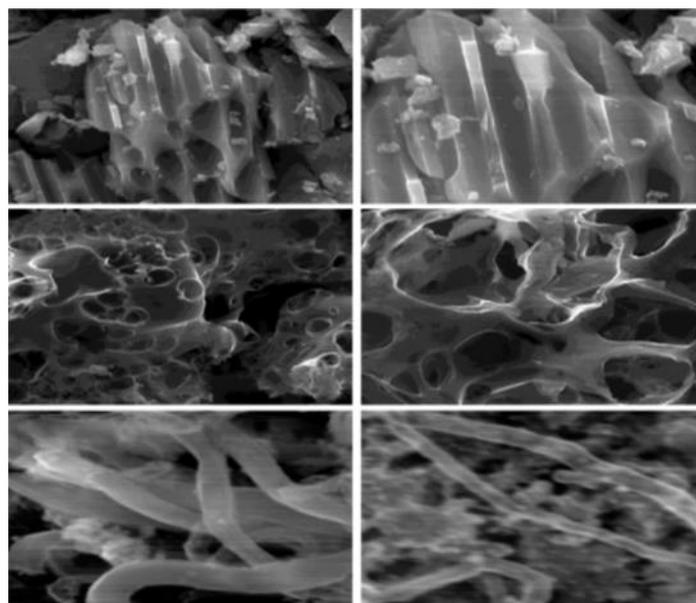


Fig. 3 SEM micrograph of prepared specimens

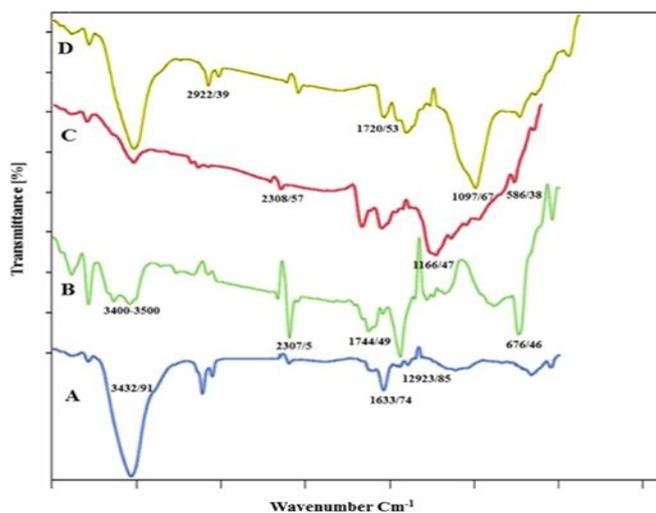


Fig. (4): FTIR analysis of specimens

#### FTIR analysis

The FTIR was done in the spectrum of the 500–4000  $\text{cm}^{-1}$  wave number scale, and the results are illustrated in Fig. 4. Consistent with Fig. 4a, the peak at the 500–4000  $\text{cm}^{-1}$  wave number scale is assigned to the stretching vibration of the O–H bond. Though, the peak at 1642  $\text{cm}^{-1}$  is assigned to the bending vibration of the uniform band. Besides, the bands of 2307.52, 1744.49, and 676.4  $\text{cm}^{-1}$  are assigned to the C–H, C=C, and C=O stretchings, in that order, in carbon nanotubes. In Fig. 4B, 3432.91 and 1633.74  $\text{cm}^{-1}$  symbolize the stretching and bending vibration of the O–H band of  $\text{H}_2\text{O}$ , which were adsorbed by AC, in that order. Besides, the peak at 12,923.85  $\text{cm}^{-1}$  is belongs to the C–H band of AC. The peak at 586.38  $\text{cm}^{-1}$  in Fig. 4C is belongs to the band between  $\text{KMnO}_4$  and, while the peaks at 1744.49 and 1166.4  $\text{cm}^{-1}$  describe C=C (the alkene group) and C–H vibration stretchings of carbon nanotubes. Lastly, in Fig. 4d, the peaks of 2922.39 and 1720.53  $\text{cm}^{-1}$  are belonging to the C–H band and C=C stretching of AC, in that order. Though, 462.60  $\text{cm}^{-1}$  is belongs to the MnO band in  $\text{MnO}_4$ . Together with the results gotten by the FTIR, the peak at 462.60  $\text{cm}^{-1}$  belongs to the MnO stretching confirmed the existence of the functional  $\text{KMnO}_4$  group. Also, Fig. 4d shows that the frequency of the C–H, C–C, and CO–H groups tended to shift to lower wavelengths which were due to the attendance of manganese and carbon functional groups. Overall, these results confirmed the presence of functional groups in MWCNTs/AC.

#### Ignitability test

Ignitability test was used to evaluate the fire retardancy of resins as varnished films. The following table illustrate the time of burning of coated plywood specimens. From the table it is clear that the time of burning plywood specimen is more than uncoated plywood specimen. It attributed to the presence of blended fire retardant additives which take long time to burn.

Limiting oxygen index	Specimen s
21%	Control specimen
40%	Specimen tested

The weight loss occurred in three steps at (380 oC, 450 oC, and 750 oC). The first step occurred at 380 oC (-.966 mg, -11.656 percent) for examination of humidity water molecules of the specimen. The second step (450 oC) (-1.570 mg, 18.948 percent) resulted in the decomposition of organic material. The third step (750 oC) (-.565 mg, 6.819 percent) resulted in the evaluation of  $\text{H}_2\text{O}$  and gases such as CO,  $\text{CO}_2$ , and HBr. DTA curves reveal two thermal steps, one endothermic at 563.18 degrees Celsius and the other exothermic at 666.31 degrees Celsius, as well as two thermal steps, one endothermic at 563.18 degrees Celsius and the other exothermic at 666.31 degrees Celsius. The specimen's final residual weight.

#### 4. Conclusion

Food waste or vehicle rubber tyres were used to make activated carbon and carbon nanotubes. There were two different activation methods: first, phosphoric acid and later potassium. By properly up-cycling and valorizing waste lignocellulosic materials. These particles were developed that could be easily integrated and effectively dispersed into polymers. Fire tests like ignitability, limiting oxy-index, and thermal stability were carried out using wood specimen s painted with polymers where specimen s showed far extent in fire retarding.

#### References

- [1] A.Abdolmaleki, S.Mallakpour, M.Rostami Role of carboxylic acid-functionalized MWCNTs in potentially biodegradable poly(- amide-imide) nanocomposites based on N,N'-(pyromellitoyl)-bis-S-valine: preparation, thermal and morphological properties. Science vol.54,PP.53-60, 2015.
- [2] J.Acharya, JN.Sahu, CR.Mohanty, BC.Meikap, Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. Science vol.149, pp.249-262, 2009.
- [3] M.Adam, R.Ocone, J.Mohammad, F.Berruti, C.Briens ,Kinetic investigations ofkraft lignin pyrolysis. Science vol.52, pp.45–54, 2013.

- [4] A.Arampatzidou, E.Deliyanni, Comparison of activation media and pyrolysis temperature for activated carbons development by pyrolysis of potato peels for effective adsorption of endocrine disruptor bisphenol-A. *Colloid Interface Sci*, vol.466, pp.101-112, 2016.
- [5] R.Baughman, Carbon nanotubes-the route toward applications. *Science*, vol.297, pp.787-792, 2002.
- [6] D.Bhattacharjya, H.Park, S.Kim, S.Choi, Nitrogen-doped carbon nanoparticles by flame synthesis as anode material for rechargeable lithium-ion batteries. *Langmuir*, vol.30, pp.318-324, 2014.
- [7] M.Birch, Ruda-Eberenz, M.Chai, R.Andrews, Properties that influence the specific surface areas of carbon nano-tubes and nanofibers. *The Ann of Occu Hyg*, vol.57, pp.48-66, 2013.
- [8] N.Bombuwala Dewage, R.Fowler, U.Pittman, D.Mohan, Lead (Pb<sup>2+</sup>) sorptive removal using chitosan-modified bio-char: batch and fixed-bed studies. *RSC Adv*, vol.8, pp.25-37, 2018.
- [9] A.Bridgwater Fast pyrolysis processes for biomass. *Appl Pyrolysis*, vol.5, pp.30-22, 1999.