Modified Thermal Insulator

Ali Aziz Abbas, M.Sc. in Chemical Engineering, Foundation of Technical Education,
Technical College Musayab.

Abstract

In this search new modified phenolic resin was prepared by introducing boron and nitrogen atoms through chemical reactions. This modified resin was characterized by infra- red spectroscopy technique. The results showed that boron and nitrogen atoms presence in the resin. Moreover this resin used as matrix for carbon filler in order to prepare composite material .Thermogravimetric analysis (TGA) and the pyrolysis parameter like ablative time, erosion rate, were determined .The results showed that modified resin higher thermal stability than unmodified resin, moreover addition of carbon filler to modified resin increase the thermal stability.

الخلاصة

في هذا البحث تم تحضير راتنج فينولي مطور بواسطة ادخال عنصري البورون والنايتروجين في التركيب الكيميائي للراتنج من خلال اجراء بعض التفاعلات الكيميائية . شخص الراتنج المطور باستخدام تقنية الاشعة تحت الحمراء. واثبتت النتائج على ان ذرات البورون والنايتروجين موجوده في الراتنج . ومن ناحية اخرى استخدم الراتنج المطور كمادة اساس مع مسحوق الكاربون لتحضير مادة مركبة , حيث اجريت فحوصات التحليل الحراري الوزني,واللهب ومعدل التعرية, ودلت النتائج على ان الراتنج المطور هو اكثر ثبات حراري من الراتنج الغير مطور ,كذلك اضافة مسحوق الكاربون الى الراتنج المطور يزيد الثباتية الحرارية.

Introduction

The ablative insulating materials are defined as material used for protecting heat-sensitive structures against the damage effects of an external high temperature energy source where the structure need only to be protected for limited.

There are two general types of thermal insulation which utilized in high temperature applications:

1- Rigid reinforcement plastics.
2- Filled electrometric composites.

Although rigid phenolic insulation is being utilized the tendency is toward the use of filled elastomric materials. While phenolic insulations have out standing erosion resistance, also it has a tendency to cracked and become unbounded where used in application at high pressure temperature [(1)].

The phenolic resins are the oldest and lowest cost thermosetting polymer material. They are derived from the condensation of phenol (C_6H_5OH) and aldehyde such formaldehyde (HCHO).

This reaction was first recorded in 1872 by Bayer. However the reaction during polymerization could not be controlled till 1909, when Loe Bacland was succeeded in developing the first practical phenolic resin system**.** Then by introduction of fibers in various forms as a in forcing material with the phenolic matrix a very attractive properties of phenolic composite are upgraded to an extent that they are composite in certain applications with best of exotic steels refractory metals and other metal alloys[(2)].

The boron – containing phenol- formaldehyde resin (BPFR) is modified phenolic resin which is obtained by introducing boron to the main chine of common phenol formaldehyde resin. The (BPFR) possesses many excellent performances such as thermal stability, mechanical strength, and electric properties. But the general (BPFR) are extremely sensitive to moisture [(3, 4)].

The effect of additives such as carbon, metal oxides, phosphates and borates to novolac were studied by Aurbach. The results showed that the additives have a little effect on polymer pyrolysis [5].

Addition of carbon filler to phenolic resin was studied by Shenzhen. The properties showed more effective as a modified for ablation material [6].

Much has been done on thermogravimetry technique (TG) in order to study the kinetic parameters for thermal decomposition of phenolic composite. Rustles of (TG) curve are known to be effected by a number of experimental variables, such as heating rates [7].

Boron containing Phenolic and cardanolic polymers were synthesized by Antony and Pillai. Flammability and thermal stability of these polymers were evaluated by LOI and TG. The polymer showed better flam retardncy and high thermal stability [8].

Wang prepared a phenolic resin modified with zirconium. The chemical structure and thermal properties of the resin were characterized by IR and TG. The results showed that zirconium exists in molecular chain and higher thermal stability than popular phenolic resin [9].

Motawi, Ismail and Bad, prepared a modified poly (methacrylate) PMMA. This polymer was prepared by chain addition of methyl methacrylate MMA, in the presence of initiator and different percentages of phenolic resins. The results showed that the introducing of NPF (novolac phenol formaldehyde) enhance the electrical resistance and thermal stability [10].

In order to further improve thermal stability of phenolic resin, Duan, Geng and Yun combined boron and clay with phenolic resins. Thermogravimetric analysis showed that thermal decomposition temperature (Td) for boron containing nanocomposites was much higher than the corresponding nanocomposites without boron [11].

Theory

Phenol – formaldehyde resin:

More than a century has passed since the discovery and commercial exploitation of phenol formaldehyde (phenolics) resin [12].

Phenolic resins play a significant role within the polymer industry providing a diver rang of products within an equally divers rang applications [13].

Phenolic resin (PR) is well known for thermal resistance, dimension stability, flam retardation and superior ablative properties. However brittleness of (PR) is the main drawback that restricts its wide application [14].

Phenolics are the original synthetic plastics marked under the trade name Bakelite. The phenol formaldehyde resins are used in conjunction with carbon or silica fibers reinforcements in ratios of approximately 35 – 40 wt % resin and 60-50% fibers [15].

In industry phenolic resin reactions are usually carried out in two separate operations. The first operation involves the formation of a low molecular weight, fusible, soluble pre-polymer resin. The second operation involves curing reaction which lead to the final infusible cross-linked product[16].

Two distinct classes of phenolic resins exist namely novolac and resol. The major differences between these two classes are the formaldehyde to phenol (F: P) ratio and the type of the catalyst used [17].

In order to convert novolac into net work polymers (i.e. cure) is required hexamethylene tetramine, but resol is cured by heat only [18].

Phenolic resins are commonly used as molding compounding in foundry, spray insulations, lacquers and varnishes [19].

Theory of Ablative Phenolic Composite:

The term ablation refers to the process of sacrificial loss of insulating surface material to limit heat absorption. Ablative materials are normally used to protect structures from very high temperature that would melt metals. Among the common plastics the phenolic resin gives the highest yield of char during thermal pyrolysis. As heating progresses the outer layer of polymer may become viscous and then begins to degrade producing a foaming char. The char is a thermal insulation the interior is polymer. During percolation the volatile materials are heated to very high temperatures with decomposion to low molecular weight species which are injected into the boundary layer of gases. This mass injection creates a blocking action which reduces the heat transfer to the material.

Thus a char forming resin acts as a self-regulating ablation radiation providing thermal protection through transpiration cooling and insulation [20].

Charring polymers:

Stable polymers decompose on heating and leaves carbon char. The amount of char is a function of ring content in the structure, carbon ring that is chemically bonded at two or more sites will usually remains as char fig (1) [21].

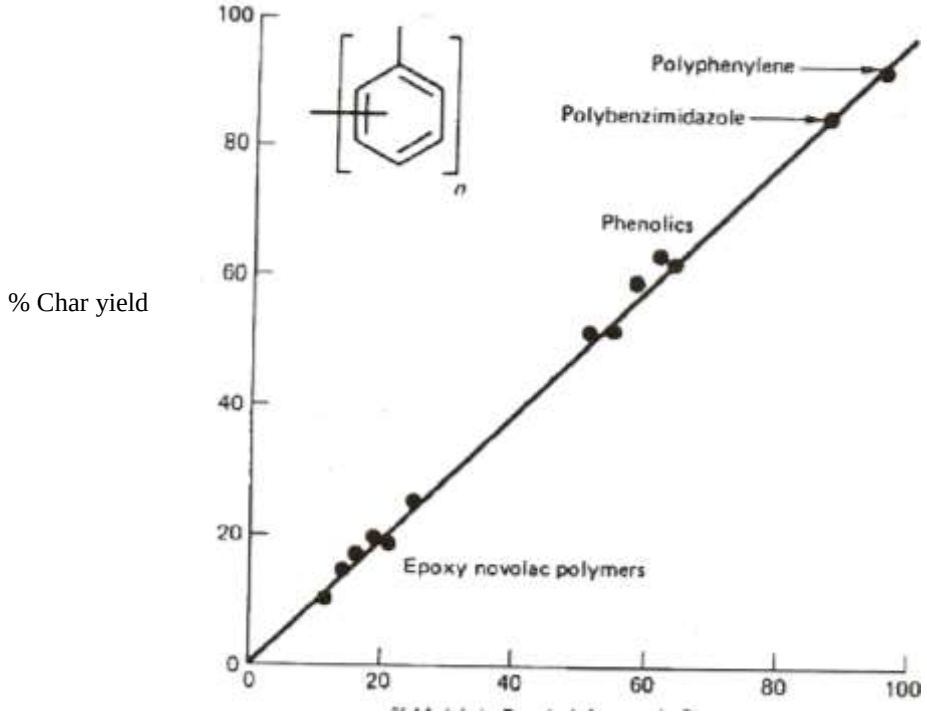


Fig.(1): Correlation of chare yield with molecular structure.

Experimental work:

A three- necked round bottom flask equipped with mechanical stirrer thermometer and condenser was charged with boric acid (1mol) and p-aminophenol (3mol). The reaction mixture was refluxed in boiling xylene for (15hr) a tris p-aminophenylborate suspension product was formed. Then excess formaldehyde was added at 80ºC with added phosphoric acid (0.1 %) as acidic catalyst (from weight of tris P- aminophenlborat). A red solid product was formed then the product with melting point 105ºC was derided and characterized by IR.

Preparation of resin with filler:

1- Preparation mixture of (novolac- HTMA). Novolac was divided into a small species and was milled by using a mortar. The powder which had been produced from pre-step would be sieved by mesh less than 100 µm. Then HTMA was milled and mixed with novolac in weight percent.
2- Prepared novolac was mixed with carbon filler.

Measurement and techniques:

Infra-red spectroscopy (IR):

The IR absorption spectra of the resins were recorded from 4000 – 400 cm^{-1} region as thin film on KBr disc.

Thermogravimetric analysis (TGA) were used in this search by taking (5-8) mg of the cured resins and exposed under programmed heating rate of 200 ºC/min under inert atmosphere (N_2 gas)

Ablative test:

This test was done according to ASTM NO E285-70

Erosion rate:

The erosion rate was calculated by dividing the original thickness of specimen by the time to burn through as follows [22]:

$$E = \frac{d}{B}$$

Where: E = Erosion rate mm/ sec
d= Thickness of specimen (mm)
b= Burn through time (sec)

Results and Discussion:

The Resin was prepared as follows:

Boro amino phenol formaldehyde. This was developed by reacting para amino phenol with boric acid and the resulting compound was reacted with formaldehyde.

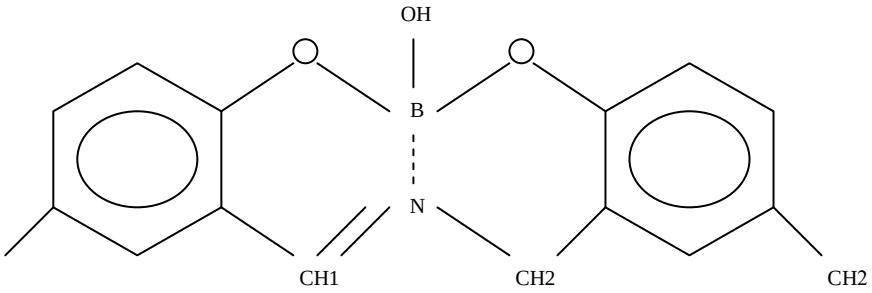


Fig (2): Boro amino phenol formaldehyde molecule

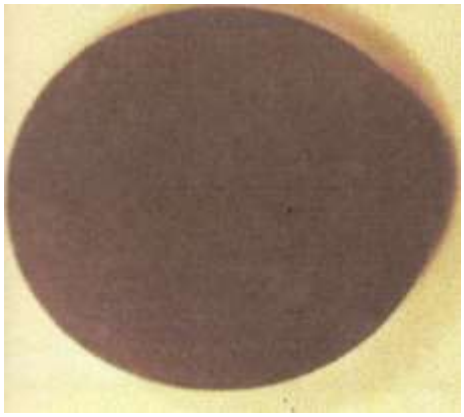
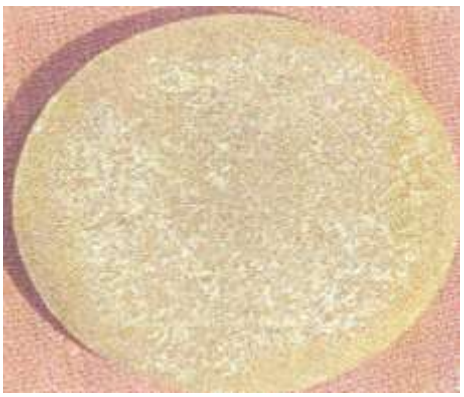


Fig (3): Resin prepared (II)



fig(4): Original resin(novolak) (I)

The above developed and original resin fig (3) and (4) respectively were carefully investigated by IR- spectroscopy in order to identify the chemical groups present in polymer, The IR spectrography are shown in fig (5)and(6) and the wave number values of peaks are listed in table (1)

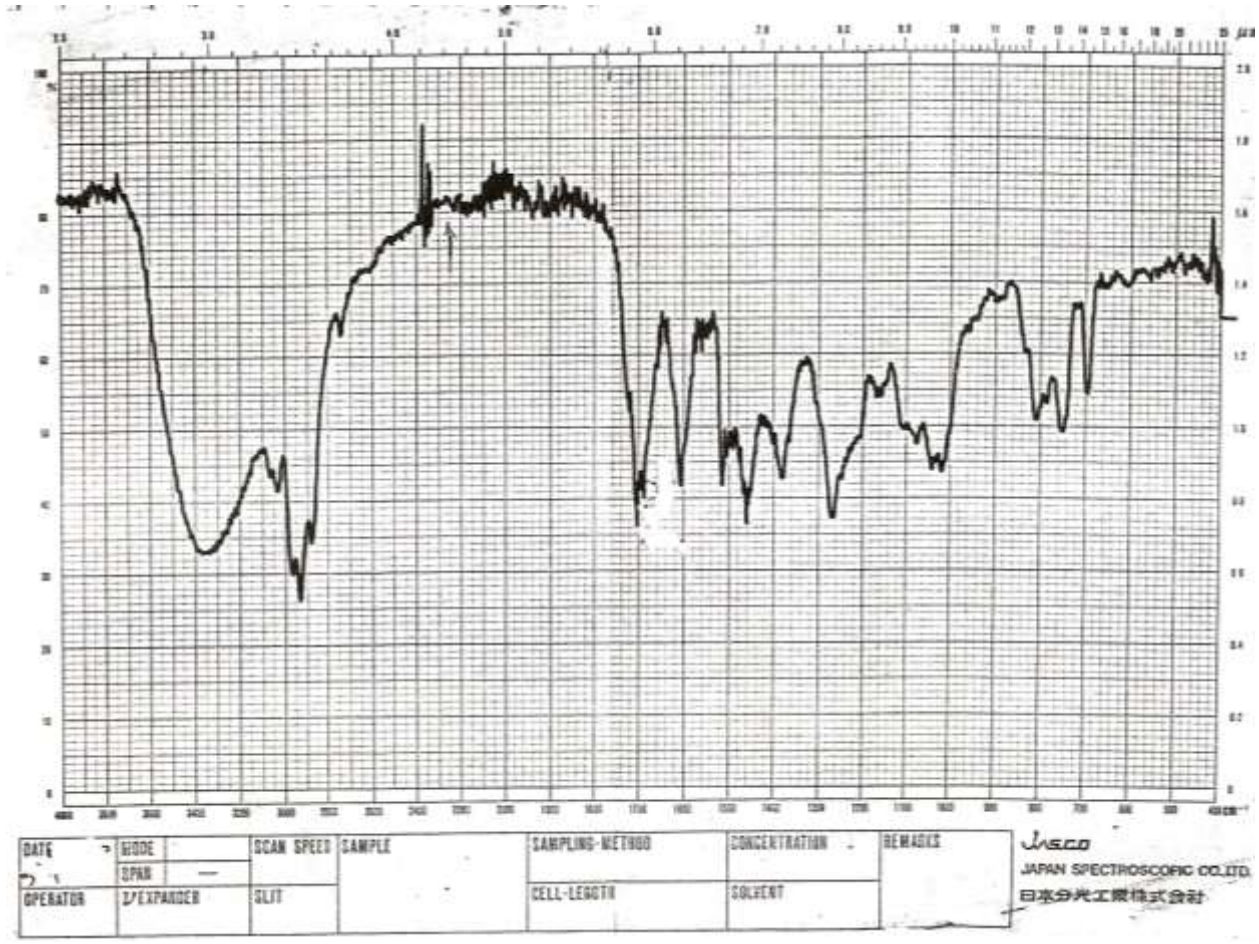


Fig (5): IR spectrography of modified resin

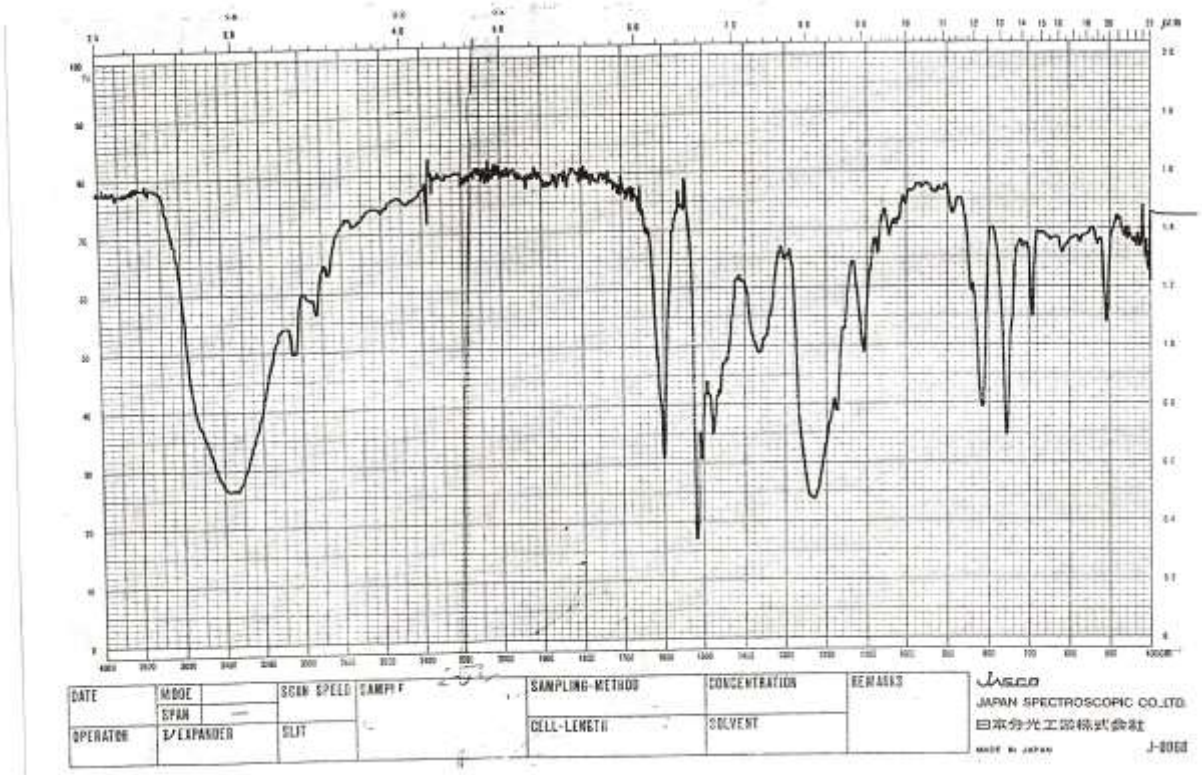


Fig (6): IR spectrography of original resin

Risen	OH	C-H	C-C	C-O	C=N	B-O	Ar-C-H
Original	1600	2825	1515	-	-	-	3025
Prepared	1600	2945	1515	1700	1690	1420	3025
Characteristic bound	sp	s	s	s	s	s	s

Table (1): The I.R characteristic bonds and their location for resin in cm^{-1}

From this data one may conclude that the proposed modified of the chemical structure is valid due to the observed characteristic bounds are associated with B—O. C=N are not present in the reference spectrograph of the pure novolak. This material may be utilized as thermal insulators at high temperature, and they act as sacrificial material which gets ablated in order to protect the metallic. Charring may be associated with the insulates evolution of some heavy gaseous layers which may act as protective boundary layer; such an observation is made by performing a detailed thermogravimatery (TGA) investigation. The resulting

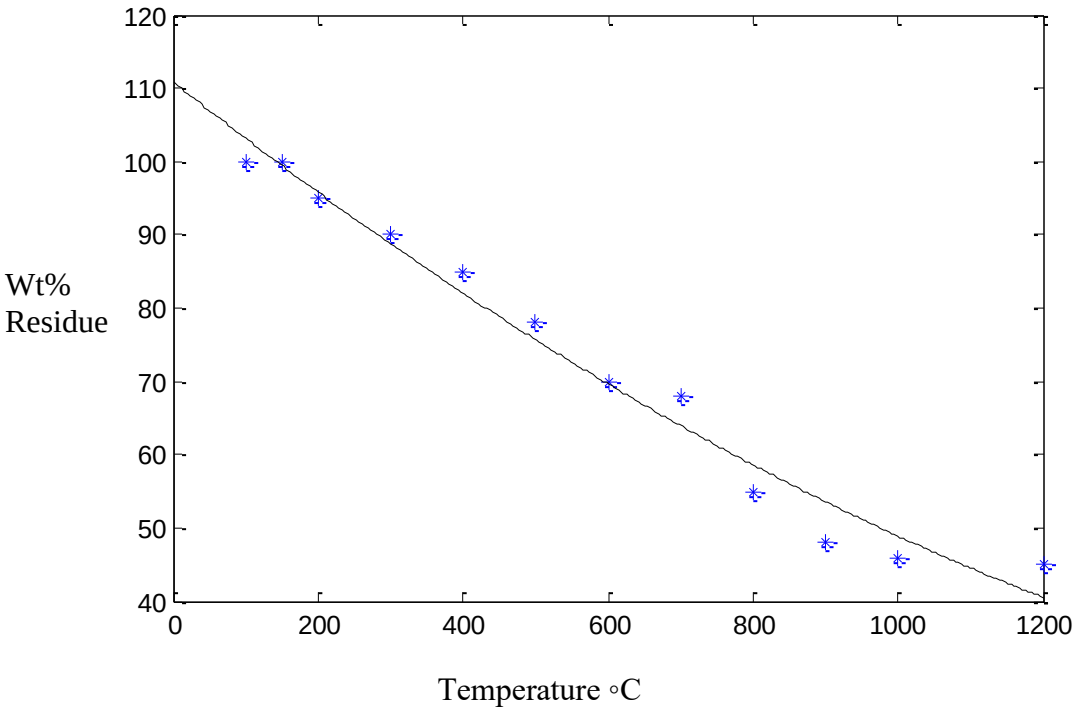


Fig (7): TG A thermogram for original resin

Thermogrammes as shown in fig (7) (8) in the modified resin the ultimate weight loss has not exceeded 35 % of the original starting weight and novolak resin weight loss 55 %.

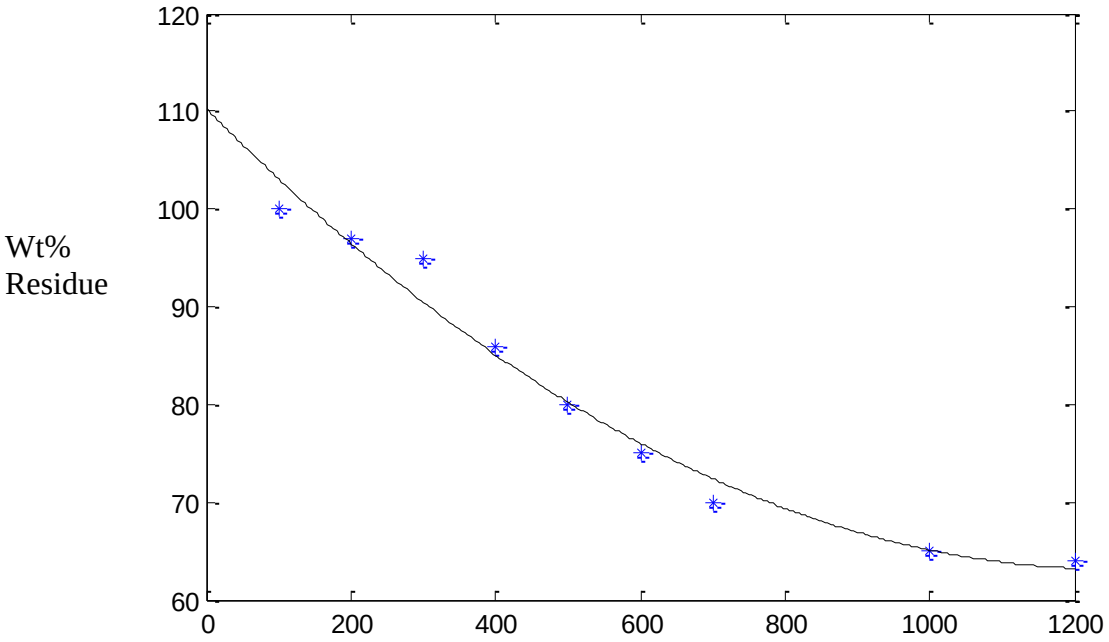


Fig (8): TGA thermogram for modified resin

Now the presence of carbon black would constitute a dispersion type composite whose thermogravimeteric behavior is shown in fig (9). It is shown addition of this filler has reduced the weigh loss.

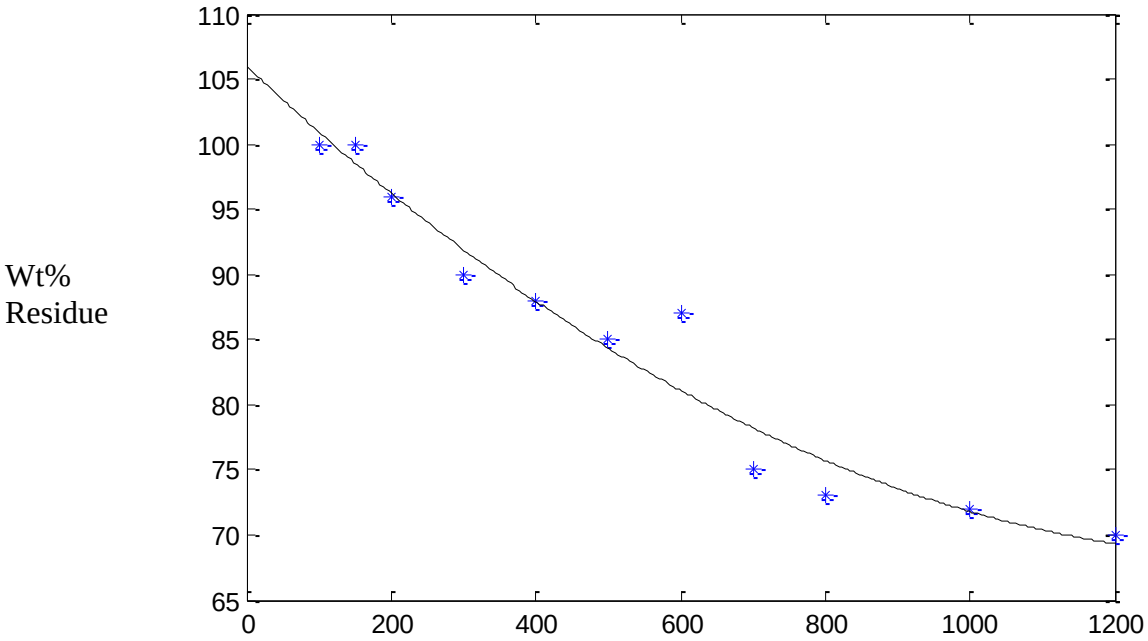


Fig (9): TG A thermogram for resin with carbon

This may support the proposed of Lum [23], who suggest that filler like carbon would enhance the charring mechanism which would leave more mass behind.

The original, modified resin and resin with carbon were subjected to oxyacetylene- flame test the details of the constituents are listed in the table 2. The exposure time varied between 32- 100 sec

. We can see the erosion rate of the modified novolak is greater than original novolak and the carbon would give a good result.

Type of resin	Filler wt%	Thickness mm	Ablative Time sec	Insulation Index sec/mm	Erosion time sec	Erosion rate mm/sec
Modified resin	-	6	51	8.75	60	0.1
Resin with carbon	30	6	94	15.61	100	0.2
Novolak	-	6	24	3.575	32	0.06

Table (2): The result of the experimental work

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