

ISOLATION BEHAVIOR OF METAL MODIFIED NOVOLAC RESIN

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ABSTRACT

Two modified phenolic resins had been prepared laboratory by introducing two different metal ions (silicon and carbon) to its structure.

The prepared modified reins had been examined by infrared to ensure the existence of the two metal ions.

In order to improve the performance and the mechanical properties of the modified resins, filler materials in different portions with carbon and fiberglass had been used. The tested insulators had been subjected to a flame test with two different firing temperatures, 2500°C and 1400°C and for two different time of exposure (1 min and 3 hrs). The prepared insulators are also thermogravimetrically tested.

A comparison study had been carried out for the products through x-ray and so suggested that the firing period and firing temperature are of prime important.

INTRODUCTION

The ablative materials are used to protect heat-sensitive structures against the damage effects of an external high temperature source, when the structure needs only to be protected for limited time. In rockets, the basic function of the insulator is to prevent the case wall temperature from exceeding some maximum value, depending on the wall materials^[1].

Two general types of thermal insulator are utilized in high temperature applications: Rigid reinforced plastics, and Filled elastomeric compositions. Although, rigid phenolic insulators are utilized, the tendency is toward the use of filled elastomeric materials. While phenolic insulation has outstanding erosion resistance, it also has a tendency to crack or become unbounded, when used in application of high pressure and temperature^[1].

Phenolic resins are the oldest and lowest cost thermosetting plastics (polymers), which are derived from the condensation of phenol and aldehydes.

When material ablated, several changes are happen: thermal decomposition by using up the heat of the process, and blocking prevent much of the heat input from reaching the surface i.e. gaseous products will thicken the boundary layer, and reducing the heat transfer^[2]. The surface may reach to a high temperature, then it re-radiates the heat back out^[3].

The ablation process to be effective, the following requirements must be involved: (1) Producing large quantity of gas when heated, (2)

the melt flow must not lead to loss of material, (3) Resisting shears and pressure forces without excessive removal, (4) Resisting chemical removal (oxidation), (5) Providing good thermal insulation, (6) Resisting thermal and mechanical shock.

ABLATION THEORY AND ABLATIVE MATERIALS

The ablation process is a combination of surface melting, sublimation, evaporation, decomposition in depth, and film cooling. As shown in Fig. (1) progressive layers of ablative materials undergoes endothermic degradation, in which the physical and chemical changes absorb the heat.

While some of the ablative material evaporates it leads to formation of enough charred and porous materials affecting the geometry and surface integrity^[3].

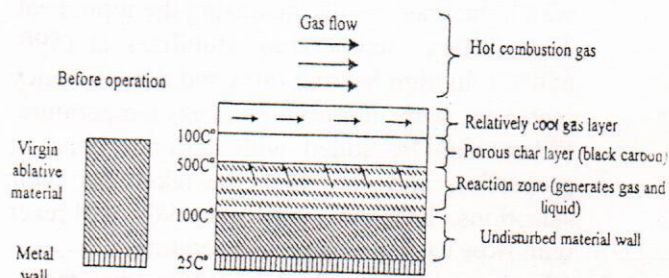


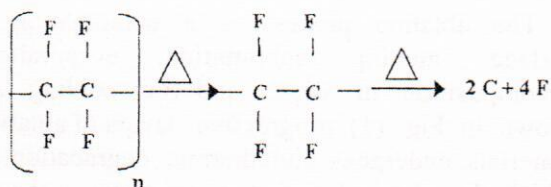
Fig. (1) Zone in ablative materials

When the thermosetting resins are subjected to high temperature, several familiar thermal decomposition pyrolysis, char formation, and evaporation occur according to the thermal induced mechanism. While oxidation results from the chemical interaction of the ablator of the surrounding atmosphere^[3].

The analysis and experimental investigation of ablation process indicate that the ablative materials acts like any thermal heat sink. But in the poor conductivity it causes rapid temperature rises (650-850°K) to the surface. Then, the resin decomposes endothermally into a porous carbonous char and pyrolysed gases. As the char depth increases, these gases undergoes an endothermic cracking process as they percolate through the char in a counter flow direction to the heat flux. These gases then form an interfacial fuel-rich boundary layer over the char^[1].

Materials that decompose into low molecular weight fragments should produce high volume of gases. These compounds have usually high heat of decomposition as a result of chemical bond breakage during the process of decomposition^[4].

Ablative performance is directly related to the heat of decomposition. Teflon for example will break to its monomer. At very high temperature additional break down will take place that absorbs more heat.



The above reaction absorbs for blocks 100-550J/g in ablative application^[4]. Ablative materials can generally be broken down into:

1. Subliming ablaters, which vaporize without loss in melting for example teflon. It becomes soft above 371°C, it does not melt or flow. Instead, it vaporizes or polymerizes at rate, which increase with increasing the input heat. The surface temperature stabilizes at (590-650°C) in high heating rates and the efficiency increases with increasing the gas temperature. Fillers may be added with teflon to improve properties, and care must be taken for their selections, because many materials will react with flow carbon at high temperature^[4].
2. Charring ablaters, which have two advantages over sublimates. Firstly they build up a char layer, which remains as insulator after

carbonization. Secondly, the char temperature will rise to a level where it radiates a significant amount of heat out to the space. Charring in organic resins is controlled by the percentage of cross-linked rings in the surface. For example, phenol will lose hydrogen, oxygen, and methyl group on heating^[4].

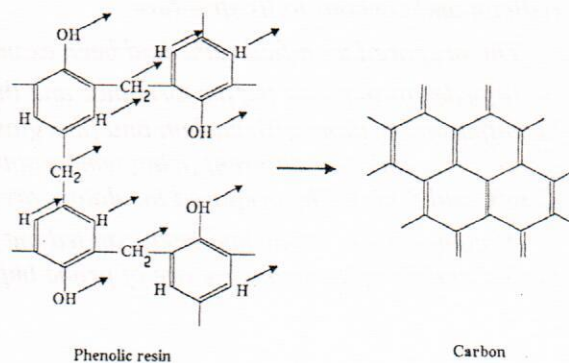


Fig. (2) phenolic resin converted to carbon

Three distinct layers can usually be found in charred ablative samples, they are explained below in Fig. (3).

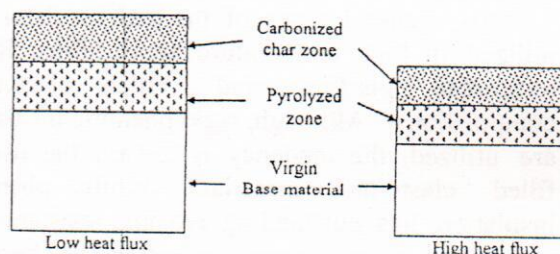


Fig. (3) Charred ablator cross-section

At low heating rates a thick char layer is formed. The carbonized zone is primarily porous carbon, which may contain silicon or other fillers. The pyrolyzed zone consists of ablative materials, which may have been darkened, or partially carbonized. The overall thickness may be more than the original thickness because of swelling, or may be less due to the material loss^[4].

High heating rates usually consume the surface materials, including the char, and loss in mass due to the combination of vaporization, erosion and oxidation operations. Char and pyrolyzed zones are thinner than that formed in the case of low

heating rates^[4]. Erosion loss is reduced by using high temperature fiber reinforced such as silica or carbon.

Oxidation may also be limited by the oxidation of silica, and at very high temperature, silica and carbon will combine to form an oxidation resistant layer of silicon carbide^[4].



Phenolics have been pointed to be basic resin system for ablative materials, they yield specifically good char, but they require high molding pressure and in the same time they are brittle.

Phenyl silanes are copolymers or mixture of silicon and phenolic resins, which offer advantage over plain phenolics. They give good char and yields silicon carbide during ablation. On the other hand phenolic nitriles have a good thermal and mechanical shock resistance and can be molded at low pressure. While rubber nitriles rubber have standard insulation for solid propellant rocket motor. Another example is the silicon rubber, it has the ability to be used for medium heat flux of early manual re-entry vehicles to serve environments such as rocket nozzles exit zones.

Silicon resins don't form carbon char, and in the presence of oxygen they give silicon dioxide, they have high elongation even at temperature down to (-100°C).

Finally, novalic epoxies offer higher char forming properties than do the bis-phenolic resins. Their structures have high cross linked density and high aromatic ring content. Ablative use of novalic epoxies is limited because they don't produce chars as phenolics^[5].

Fillers and reinforced materials are used in ablative formulation to improve the performance. Low density fillers reduce strength, erosion, and improve the char formation.

Testing the prepared Insulators

1. Infrared test (IR): Novalic, boron modified and silicon modified phenolic resins more examined by IR spectral photo meter type JASSCO IR-610 as thin layer film using NaCl and KBr cells.
2. Thermal analysis: The kinetics of thermal decomposition for both pyrolysis and carbon formation of resins samples (with and without

filler) were investigated using thermogravimetric analysis (TGA). The manufacturing procedure consist of mixing filler (carbon, graphite) powder with the resin (10% by weight HMTA added) then heated at 50°C for three hours and cured at 80 bar at temperature range (160-200°C), the diameter of the sample 2.5-4 cm and thickness 2-4 mm.

3. X-ray diffraction test: Standard Phillips types PW-1877 automated powder diffractometer was used with Cu k α radiation.

RESULTS AND DISCUSSION

The modified resins were carefully investigated by IR spectroscopy to identify the existence of substituted ions. The IR specters are shown in Fig. (4, 5, and 6) in which Fig. (4) give the IR specter of pure novalic resin while Fig. (5) and fig. (6) give the IR specters of modified novalic with boron and silicon respectively.

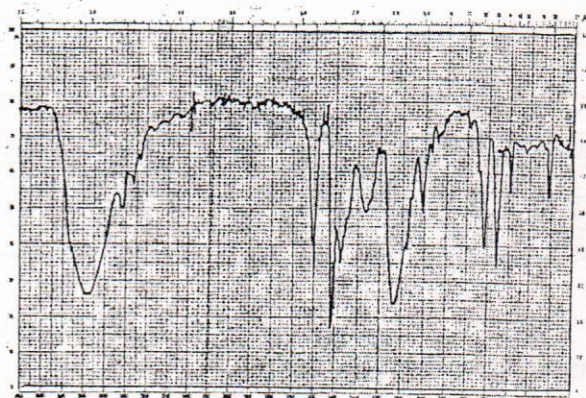


Fig. (4) IR spectra of novalic resin

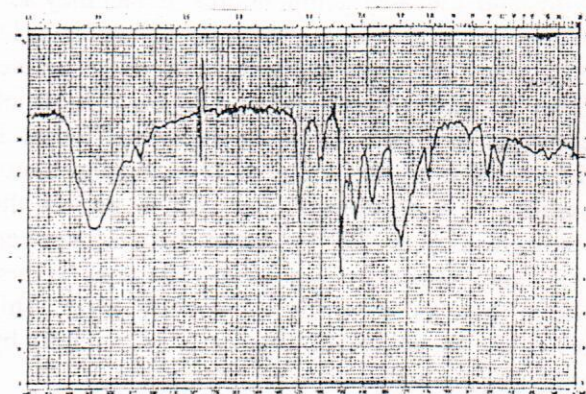


Fig. (5) IR spectra of boron modified resin

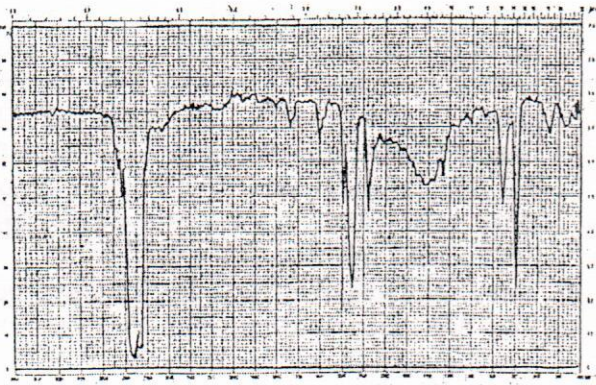


Fig. (6) IR spectra of silicon modified resin

The data of the wavelength which ascertain the existence of B-O and C-Si bond are given in Table (1). From Fig. (4, 5, and 6), and Table (1), it is seen that B-O and C-Si bonds appear in the region of 1420 and 1100 respectively while in Fig. (4) these two groups are disappeared.

Table (1) The IR characteristic bond and their location for the resins

Resin	Wavelength (λ) cm^{-1}								
	OH	C-H	C-C	C-O	C=N	B-O	Δ r-C-H	C=C	Ether
I	3350	2945	1515	1700	1690	1420	3025	1600	
II		2850	1515	1670			3025	1600	1100
III	3350	2825	1515				3025	1600	

This gives assurance of existence of these two metals in the modified novolac^[6].

In spite of the fact that all polymers are considered as very susceptible to elevated temperatures, these resins may perform contain mechanism, by which they may be able to withstand elevated temperatures. In fact they acts as sacrificial materials, which get ablated in order to protect the metallic frame work of the surface. Such sacrifices may involve heat transfer, which consume or block some of the available heat. It may involve the development of a charring ablator yielding a vary porous char, which protect the framework from the generated heat. More over, this may associate with heavy gaseous layers, which act as protective boundary layer. This behavior is shown in figures (7, 8, and 9) by exposing the materials to high temperature.

A comparison between the three thermograms lead to the fact that least sacrificial is exhibited by boron modified resin in where the ultimate weight loss has not exceeded 50% and novolac 60% and

then silicon modified which loss almost 98% of its weight. The comparison had indicated the role played by the resin during the thermal exposure process.

The maximum weight loss was in silicon modified, actually takes place at much lower temperature than those exhibited by the other resins.

The presence of fillers like carbon black and graphite would constitute a dispersion type composite whose gravimetric behavior is shown in Fig. (10). It is shown that the addition of equal amounts of carbon and graphite powders was largely reduced the weight loss. This was supported by the proposal of Lum, who suggest that the filler like carbon and graphite would enhance the charring mechanism, which would leave more mass^[7].

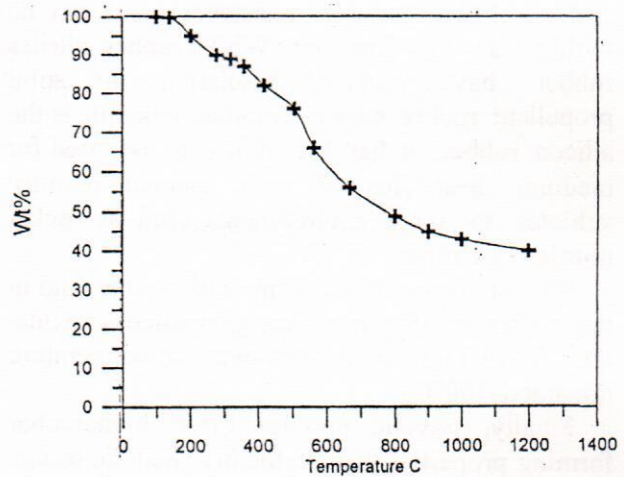


Fig. (7) TG thermogram for novolac

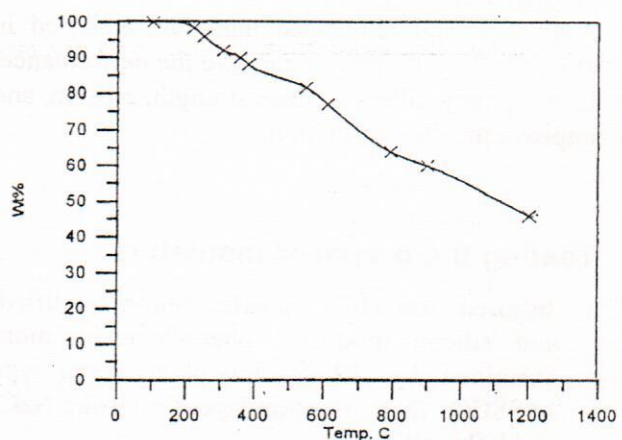


Fig. (8) TG thermogram for carbon modified resin

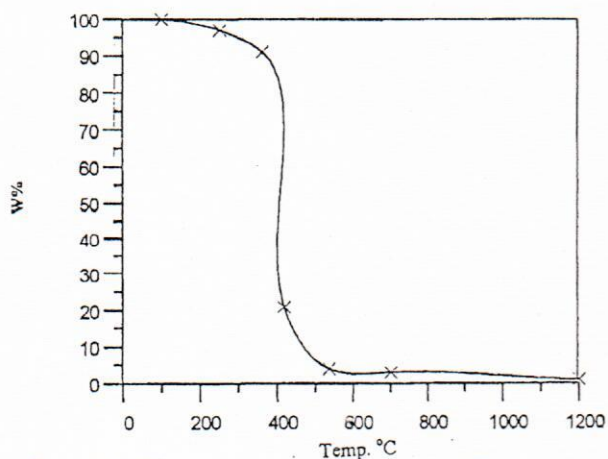


Fig. (9) TG thermogram for silicon modified resin

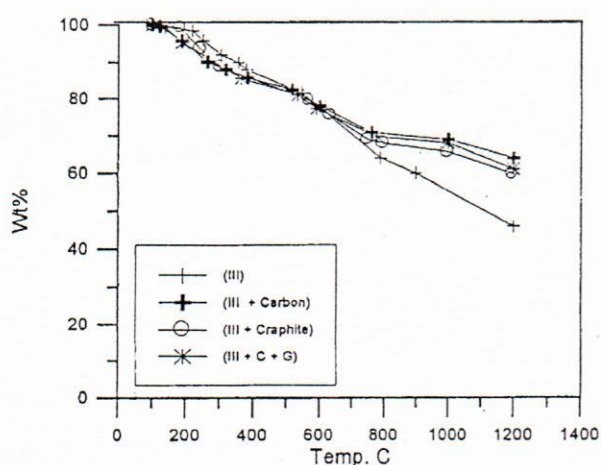


Fig. (10) TG thermogram for carbon modified resin with fillers (carbon + graphite)

The above conclusion was also ascertained by x-ray diffractogram of boron modified, which appear in Fig. (11a, 11b).

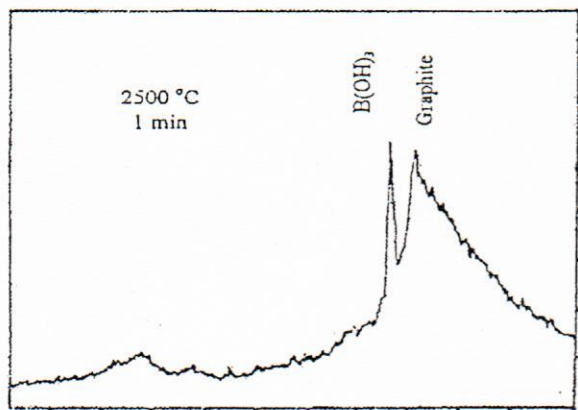


Fig. (11a) X-ray diffractogram for carbon modified resin (2500°C for 1 min)

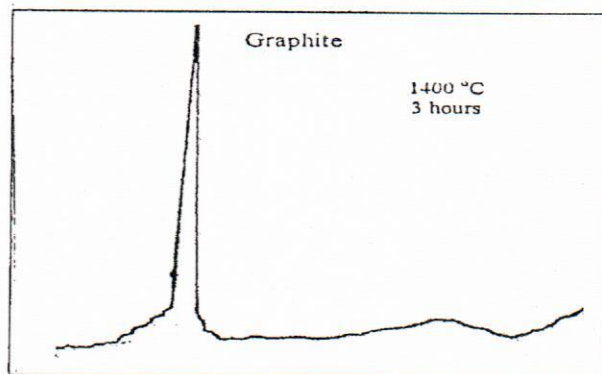


Fig. (11b) X-ray diffractogram for carbon modified resin (1400°C for 3 hrs)

This suggesting that the firing period is of prime importance. Moreover in most diffractograms a peak of boron oxide or hydroxide is present. Due to the presence of catalyst It is interesting to improve the performance characteristic of the insulator, concentrate on composite resin rather than pure resin to achieve composition of resins which gave much better control on light temperature behavior.

CONCLUSIONS

1. the type of introduced ionic groups judges the behavior of the resin (charring, erosion, and insulation index).
2. The boron ionic groups acts as strong catalyst to reduce the graphitization time.
3. The presence of the fillers would heavily modify the heat resisting process of the resin.
4. Introduced metal ions modify the heat and flame resistance of the phenolic rings.

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