

# **THERMOSETTING ISOIMIDE RESINS**

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## THERMOSETTING ISOIMIDE RESINS

Thermosetting matrices have been widely used in fiber reinforced composites and occupy the largest market share of this type of material. Their inherent characteristics like ease of processing, excellent thermal and dimensional stability and good resistance to solvents are the greatest advantages in comparison to thermoplastic matrix materials. This makes thermoset matrix materials the preferred choice for use in composites. The development of thermoset polymer matrix fiber reinforced composites brought a revolution in light weight structural materials mainly in aerospace applications.

Polyimides, particularly aromatic polyimides (Figure 1) are one of the most important classes of high performance polymers [1,2] with a combination of exceptional mechanical, thermal, electrical and optical properties along with chemical and solvent resistance [3,4]. The excellent combination of properties makes them suitable for a wide range of applications, from engineering plastics in aerospace industries to membranes for fuel cell applications and gas or solvent separation.

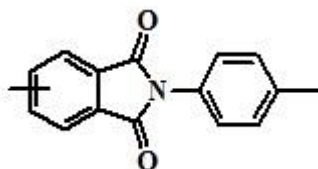


Figure 1 Structure of polyimide

Thermosetting resins based on ethylenically unsaturated N,N'-bis(imides) on controlled polymerization leads to oligomers or prepolymers (Figure 2). The prepolymer solutions are used to impregnate fibrous materials like glass cloth or carbon fiber.

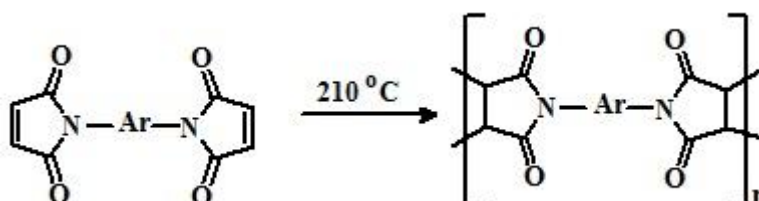


Figure 2 Thermal polymerization of bis(maleimide)

The structure of isoimide is shown in Figure 3. Thermosetting resins based on bis(isoimide) structure are rare. Polyisoimides are expected to possibly serve as novel and suitable

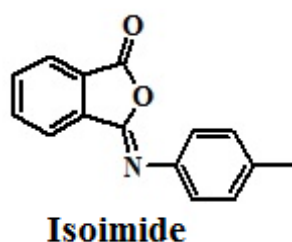


Figure 3 Structure of isoimide

precursors for polyimides with improved performance because of the transformation without producing harmful by-products like water. The solubility of bis(isoimide) prepolymers in low boiling solvents is an attractive feature for the advanced composites manufacture.

Although synthesis and some interesting properties of polyisoimides have been reported [5-7], detailed studies of thermosetting resins based on bis(isoimide) structures are rare. The commercial isoimide oligomer product, Thermid IP600, has been successfully produced via the dehydration of the oligoamic acid (Figure 4) using dicyclohexylcarbodiimide at National Starch Chemical Corporation.

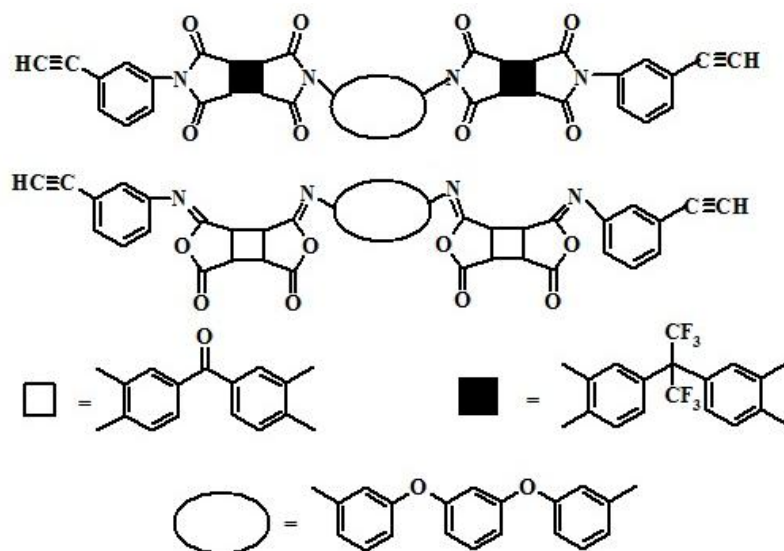


Figure 4 Commercially available Thermid resins

Compared to the amount of research work that has been carried out on imides and polyimides, the work pertaining to isoimides and polyisoimides are considerably limited.

## CHAPTER DETAILS OF THE THESIS

### Chapter 1. Introduction

This chapter deals briefly with the classification of polymers. A detailed account about polyimides is presented. Both condensation and addition polyimides are discussed. In addition polyimides, bismaleimides, bisnadimides, bisallylnadimides, benzcyclobutene resins and acetylene terminated resins are discussed in detail followed by a detailed introduction regarding isoimides.

### Scope of the present investigation

In the present research work, interest is shown in isoimide chemistry in view of developing appropriate precursors for thermosetting imides, with an expectation of synthesizing crosslinked polyisoimide networks, as well as developing versatile reactive intermediates for organic matrix resins.

Since the initial report of the isolation of an isoimide in 1893, isoimide intermediates have been proposed to occur in a wide array of reaction. Systematic studies on isoimides to fully

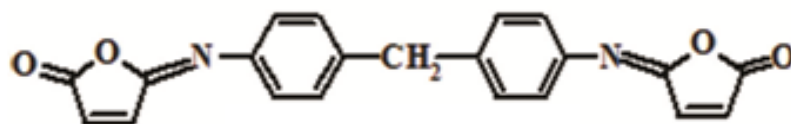
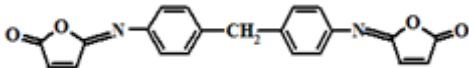
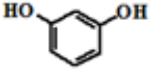

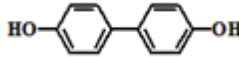
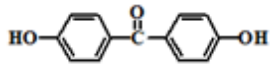
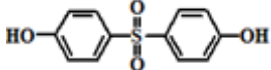
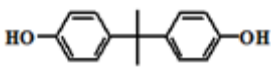
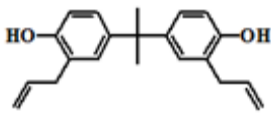
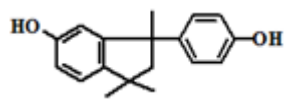
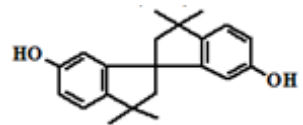
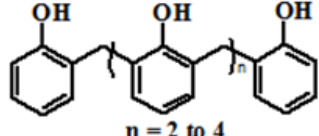


Figure 5 Structure of bis(isomaleimide) (VS)

explore the characteristic properties, however, have not been done primarily because of the instability and difficulty in preparation. Isoimides, however, can be formed under special conditions particularly by cyclization with trifluoroacetic anhydride or dicyclohexylcarbodiimide (DCC). Isoimides have been reported to be susceptible to nucleophilic addition and transformed to imides with heat or acids. Based on these facts, the following work has been planned and executed.

Blending of different diphenols (Table 1) and orthonoalac with bis(isomaleimide) (Figure 5) will change the properties like mechanical, thermal, optical and flammable properties. Thus, the author is motivated to study the thermoset polymers based on bis(isomaleimide) and their blends with structurally different diphenols.

Table 1 Structures of bis(isomaleimide) and diphenols

VS Bis(isomaleimide)	
1 Resorcinol	
2 Quinol	
3 4,4'-Dihydroxybiphenyl	
4 4,4'-Dihydroxybenzophenone	
5 4,4'-Sulfonylbisphenol	
6 4,4'-(Propane-2,2-diyl) diphenol	
7 2,2'-Diallylbisphenol-A	
8 5-Hydroxy-3-(4-hydroxyphenyl)-1,1,3-trimethyl indane	
9 6,6'-Dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane	
ON Ortho novalac	

In order to achieve the set goals, it is planned:

- To synthesize, characterize and study the curing behavior of bis(maleimide) and bis(isomaleimide) based on 4,4'-diamino diphenyl methane.
- To blend bis(isomaleimide) with nine different diphenols and study the thermal polymerization behavior using DSC
- To thermally cure above blends and study their thermal degradation behavior using TGA
- To investigate the thermal degradation kinetics of the polymers by more recent model free kinetic methods recommended by International Confederation of Thermal Analysis and Calorimetry (ICTAC) viz., Corrected Flynn-Wall-Ozawa (C-FWO) Method, Corrected Kissinger-Akahira-Sunose (C-KAS) Method, Advanced Vyazovkin (A-VYZ) Method and Friedman Method
- To study the evolved gases during thermal degradation of these bis(isomaleimide) diphenol blends using TG-FTIR technique to have an idea regarding the products formed during thermal degradation.
- From the above investigations, to blend bis(isomaleimide) with one of the diphenols (bisphenol-A) and an ortho novalac in different ratios and investigate in detail the thermal curing behavior using DSC.
- To evaluate the thermal stabilities of the thermally cured above blends using TGA and study briefly the nonisothermal degradation kinetics.
- To investigate the evolved volatiles from the thermally degrading polymers prepared by blending bis(isomaleimide) with bisphenol-A and an ortho novalac using TG-FTIR technique.

## **Chapter 2. Literature Survey**

In this section, prominent results from the literature associated with the studies of curing and degradation of bis(isomaleimide) are detailed. The history of materials, chemical evolution and the status of present problems are focused. From the literature survey one can conclude that work pertaining to bis(isomaleimide) and its blends with diphenols are scarce. Further the estimation of thermal degradation kinetic parameters is also not attempted so far and this initiated the author to carry out this research work.

### **Chapter 3. Experimental**

This chapter deals with the preparation and characterization of bis(maleimide) of 4,4'-methylene dianiline (BMIM), bis(isomaleimide) of 4,4'-methylene dianiline (VS), 5-hydroxy-3-(4-hydroxyphenyl)-1,1,3-trimethyl indane (IBP), 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (SBI), 4,4'-dihydroxy benzophenone and phenol formaldehyde orthonovolac resin (ON). Blending and polymerization of bis(isomaleimide) (VS) with different diphenols and blending and polymerization of bis(isomaleimide) VS with BPA and ON are investigated in detail.

The Fourier transform infrared (FTIR) spectra are recorded using SHIMADZU-8400S infrared spectrophotometer. The cure characteristics of the synthesized monomers are studied using differential scanning calorimeter (DSC) (TA Instruments DSCQ20). The thermal stability of the polymer samples are investigated using a thermogravimetric analyzer (TGA) (TA Instrument TGA Q50). The degradation kinetics is studied using Corrected Flynn-Wall-Ozawa (C-FWO), Corrected Kissinger-Akahira-Sunose (C-KAS), Advanced Vyazovkin (A-VYZ) and Friedman (FRD) methods. The volatiles formed during the thermal degradation of the various polymers are studied using TG-FTIR and is carried out in the instrument TGA Q5000 V3.10 Build 258 purchased from TA Instruments.

### **Chapter 4. Results and Discussion**

The results and discussion section is subdivided into four parts. In the first part, the structural characterization of the BMIM and VS are presented and discussed. In the second part, the thermal studies pertaining to BMIM+BPA and VS+BPA blends carried out using DSC and TGA are presented and discussed. In the third part, the VS is blended separately with structurally different diphenols and are thermally polymerized. The thermal curing behavior of these blends is investigated using DSC and the thermal stability aspects are studied using TGA. The thermal degradation kinetic parameters are calculated, presented and discussed. In the fourth part, the structural and thermal curing behavior of VS+BPA+ON blends investigated using FTIR and DSC are presented. The thermal stabilities of the polymers are studied using TGA and the calculations of the apparent activation energy for the thermal degradation ( $E_a$ -D) and pre-exponential factor (A) of these materials are also included. Based on the TG-FTIR results, an insight into the structural aspects of these polymers is provided.

#### **4.1 Structural aspects of BMIM, VS and their polymers: FTIR studies**

The presence of the bands corresponding to C=C stretching of the phenyl nucleus ( $1388\text{ cm}^{-1}$ ), C=C stretching of the imide ring ( $1512\text{ cm}^{-1}$ ) and cyclic imide -OC-N-CO- stretching vibration ( $1712\text{ cm}^{-1}$ ) in the FTIR spectrum of BMIM confirmed its structure. In the FTIR spectrum of the bis(isomaleimide) VS, the band present at  $888\text{ cm}^{-1}$  is due to the isoimide ring vibration and another band noted at  $1820\text{ cm}^{-1}$  is assigned for the lactone carbonyl group. Both these absorptions are characteristics of isoimides in general. The FTIR spectrum of thermally cured BMIM shows the absence of maleimide =CH band at  $3095\text{ cm}^{-1}$  and presence of an aliphatic C-H band at  $2931\text{ cm}^{-1}$ , which indicates the polymerization of the maleimide double bond. Thermally polymerized materials (Poly BMIM and PolyVS) show a band at around  $1705\text{ cm}^{-1}$  confirms the presence of the cyclic imide ring structure in the cured thermosets. The thermally polymerized VS shows new absorption bands at  $3444$  and  $1177\text{ cm}^{-1}$  which are assigned to N-H (amide) and -C(=O)-O- (ester) stretching vibrations, respectively.

#### **4.2 Thermal studies of BMIM, VS and their blends with BPA**

The curing behavior of BMIM, VS and their blends with BPA is examined by DSC. The onset of curing for VS and BMIM are noted around  $162$  and  $173\text{ }^{\circ}\text{C}$ , curing attained a maximum at  $232$  and  $229\text{ }^{\circ}\text{C}$  and ended at  $300$  and  $303\text{ }^{\circ}\text{C}$  respectively. The values of  $\Delta H_c$  are  $125$  and  $160\text{ J g}^{-1}$  and the temperature region of curing window is  $138$  and  $130\text{ }^{\circ}\text{C}$  for VS and BMIM respectively. From these data it is found that both VS and BMIM undergo similar type of curing process and there is only a slight variation in all the parameters calculated. Compared to the neat resin (VS), the blend (VS+BPA) shows reduction in the curing window by nearly  $17\text{ }^{\circ}\text{C}$ . The thermal behavior of the monomers BMIM and VS is different and is reflected in their blends with BPA. The thermogravimetric studies of poly BMIM and poly VS shows that poly BMIM is thermally more stable than poly VS. Polymers from BMIM and VS blends with BPA show considerable reduction in the thermal stability and also the degradation behavior of the polymers from the blends is much altered and complicated.

#### **4.3 Studies of bis(isomaleimide) and diphenol blends**

The blends of different diphenols with VS are prepared and thermally polymerized. The structures of all the polymers prepared are investigated by FTIR. The thermal curing behaviors are studied using DSC. The structural entity bearing the two phenolic groups has



much influence on the curing onset temperature. The thermal curing onset temperature of the blends increases as the molecular size of the diphenol increases. The highest onset value is seen for VS 9 (214 °C). The TG and DTG curves for the polymers have been recorded using TGA. The thermal degradation onset temperature and also the char value at 800 °C for the polymers resulting from the thermal polymerization of blends of bis(isomaleimide) and structurally different diphenols are less compared to Poly VS. This decrease in the thermal stability of the polymers from the blends may be due to the drastic structural difference created between the structures of Poly VS and Poly VS 1 to Poly VS 9. It is interesting to note that all the polymers from the blends show three thermal degradation stages very similar to the degradation behavior of Poly VS.

The thermal degradation kinetics of these polymerized materials is investigated using, C-FWO, C-KAS, A-VYZ and FRD methods. The polymer (Poly VS 9) from the blend of bis(isomaleimide) and tetramethylspirobiindane diphenol shows the highest Ea-D value and is attributed to the energy needed to break the stiff and bulky spirobiindane unit. The ln A parameter is also been estimated for all the investigated materials. The high Ea-D ( $\approx 200 \text{ kJ mol}^{-1}$ ) value is found to be accompanied by a high ln A ( $\approx 10^{20} \text{ s}^{-1}$ ) value and vice versa.

The thermal decomposition process is followed using TG analyzer interfaced with FTIR spectrometer (TG-FTIR). This technique is a real-time analysis and gives information at different time periods and temperature. From the results of these studies, it is concluded that more volatiles are released during the second stage of degradation. Apart from CO, CO<sub>2</sub>, phenols and substituted phenols, detectable amounts of aromatic amines like aniline are also formed during the thermal degradation of these cured materials. The polymers resulting from the blends of bis(isomaleimide)/diphenol show relatively less thermal stability due to the linear structures formed by the ring opening of the bis(isomaleimide) by the diphenol.

The presence of alternating ester and amide bonds in the polymerized materials facilitate easy thermal degradation since both these groups are amenable to thermal degradation due to the probable cleavage at the ester [-C(=O)-O-] and amide [-NH-CO-] linkages. This is the possible reason for the lower thermal stability of all the polymers resulting from the thermal polymerization of blends of bis(isomaleimide) and different diphenols.

#### 4.4 Thermal studies of bis(isomaleimide), bisphenol-A and orthonovalac blends

The blends of BPA, VS and ON are prepared in different ratios and polymerized thermally. The band present at  $888\text{ cm}^{-1}$  is due to the isoimide ring vibration and another at  $1820\text{ cm}^{-1}$  is assigned to the lactone carbonyl. Both these absorptions are characteristics of isoimide groups. A broad band is noted in the region of  $3363\text{ cm}^{-1}$  in ON and is due to  $\text{-OH}$  stretching vibration which confirms the presence of hydroxyl groups in the product. The presence of an intense band at  $3400\text{ cm}^{-1}$  noted in all polymers from the blends indicates the presence of  $\text{-OH/-NH}$  groups. Further from the FTIR spectra it is obvious that all the phenolic groups are not consumed during the thermal polymerization reaction.

The exotherm noted in the DSC is broad and is due to the occurrence of several reactions namely, isomerization of isoimide to imide, self and copolymerization of the isoimide and imide, the copolymerization of BPA and ON with the isoimide and the imide. The blend VS20ON ( $5.6\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$ ) releases the highest amount of heat during curing for every degree increase in temperature than the other blends. Thus the presence of more than two phenolic groups in ON influences the thermal curing behavior of VS.

The pure Poly VS shows a residual mass of 37 % at  $800\text{ }^{\circ}\text{C}$  and this value is nearly 30, 31 and 30 % for the blends VS20BPA, VS15BPA5ON and VS5BPA15ON respectively. This is due to the structural differences resulting during the thermal polymerization of the blends. The char residue decreased to 11 % when the bisphenol and orthonovolac are added in same amounts (VS10BPA10ON). This is attributed to the change in the structural moiety of the compound which has weak bonds capable of easy breakage during the thermal degradation.

The apparent activation energy of VS15BPA5ON progressively increases ( $145\text{-}240\text{ kJ mol}^{-1}$ ) with increasing  $\alpha$  values. The constancy noted is probably due the well-known rearrangement of the groups. The material VS5BPA15ON shows a slight increase and then the apparent activation energies ranges from  $137\text{ to }171\text{ kJ mol}^{-1}$  (up to  $\alpha = 0.4$ ). The activation energy increases ( $179\text{-}288\text{ kJ mol}^{-1}$ ) rapidly as  $\alpha$  value increases further. This material shows the highest  $E_a\text{-D}$  values. This is due to the presence of stable structural entities in the polymer which requires high energy to break the bond.

The TG-FTIR studies show the release of detectable amount of phenols (Figure 6) from the cured blends is confirmed by the increase in the  $\text{-OH}$  stretching band ( $3600\text{-}3800\text{ cm}^{-1}$ ). The

release of aromatic amine from the polymerized materials is confirmed by the appearance of bands in the region  $1200-1400\text{ cm}^{-1}$  (C-N stretching) and  $2900-3100\text{ cm}^{-1}$  (N-H stretching). The abstraction of inter and/or intra molecular hydrogens will favour the formation of aromatic amines at higher temperatures.

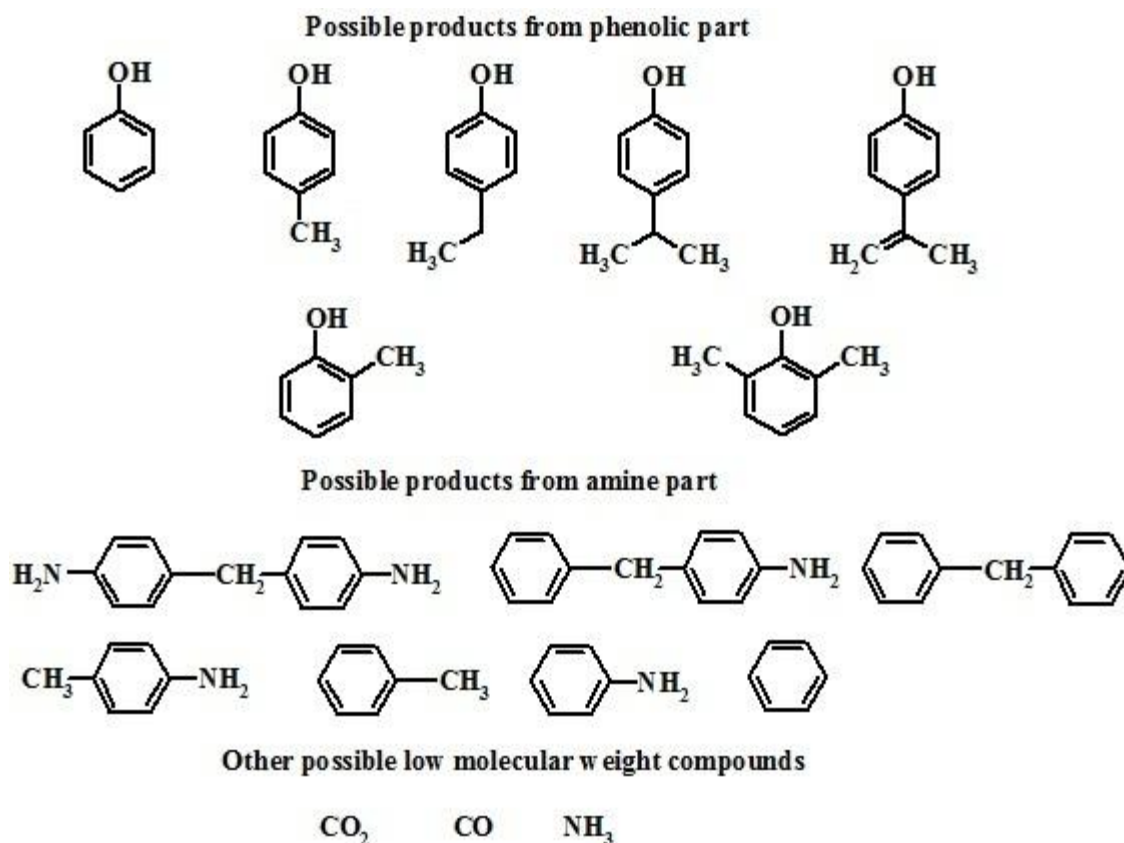


Figure 6 Possible degradation products obtained from the thermal degradation of poly VS and polymers from blends of VS with BPA and ON

From these investigations, the unique material bis(isomaleimide) can be easily prepared from maleic anhydride and structurally different aromatic diamines by using DCC as the dehydrating agent for the bisamic acid formed during the reaction. Structural modification is one of the major methods to alter both the physical and chemical properties of any system and is in competition always with the property modification by blending structurally different materials. The results of the present investigation of the blends of bis(isomaleimide) with different diphenols and phenol formaldehyde orthonovolac resin offers reduction of the processing temperature at the expense of loss in the thermal stability of the final thermoset.

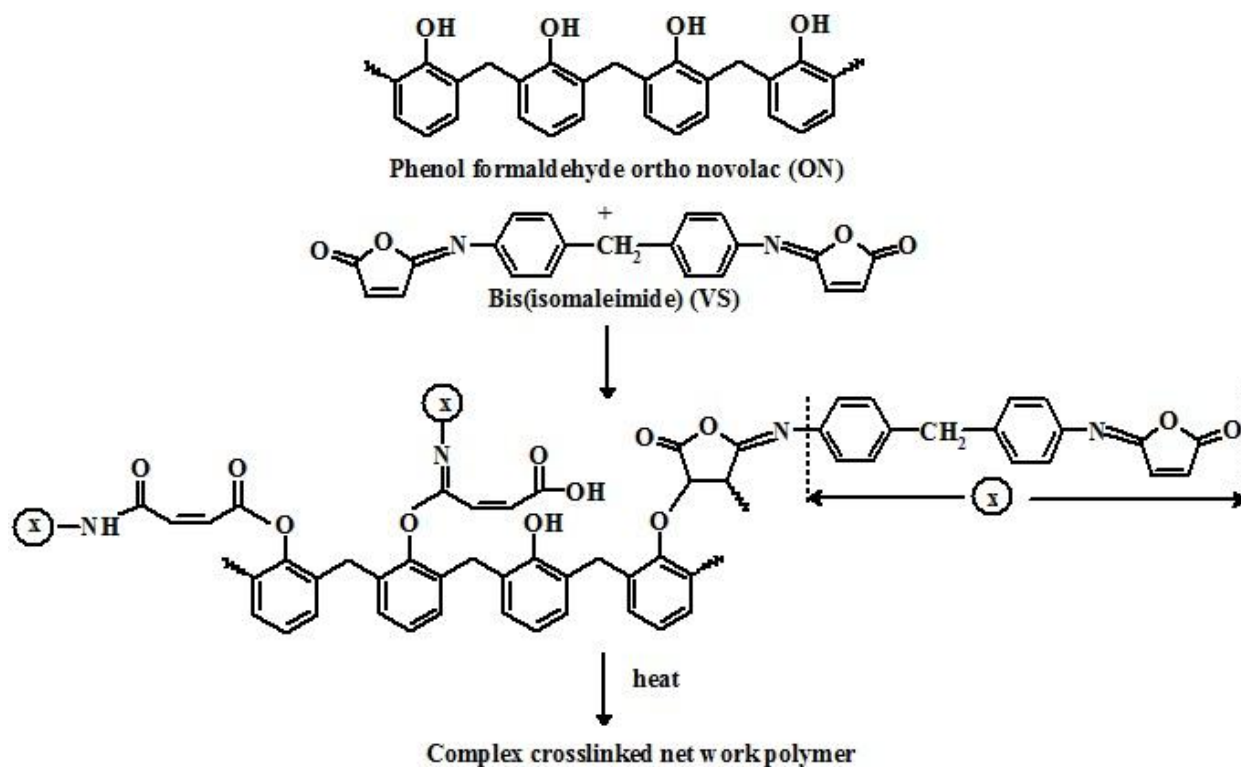


Figure 7 Structural entities resulting from the reaction of VS with ON

The most important finding from the present investigations was the presence of polyphenol in the blend of bis(isomaleimide) and diphenol enhanced the thermal stability by enhancing the crosslinking in the material. Further during the polymerization of blend of diphenol and/or polyphenol with bis(isomaleimide), the phenolic group preferable attacks (Figure 7) either the C=C or C=O group present in the isomaleimide ring and are both.

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