

DEVELOPMENT AND CHARACTERIZATION OF DOPO BASED EPOXY NANOCOMPOSITES FOR FLAME RETARDANT APPLICATION

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ABSTRACT

A study was made on the development and characterization of DOPO based epoxy nanocomposites for flame retardant application. The phosphorus containing anthraquinone diol (DOPO-AQ), phosphorous containing (DOPO-BQ) and phosphorous containing hyperbranch polysiloxane (P-HSi) was synthesized and its used as reactive flame retardant along with nanoreinforcement at various weight ratios with the diglycidyl ether of bisphenol-A epoxy (DGEBA) resin. The synthesized monomer was characterized by Fourier transform infrared spectra FT-IR.

1.1 INTRODUCTION

The epoxy resins are widely used in various industrial applications. The coatings industry is the biggest consumer of epoxy resins [1-5]. These resins are used mostly as chemical and special purpose coatings. Epoxy resins provide thin-layer durable coatings having mechanical strength and good adhesion to a variety of substrates and resistant to chemicals. They find applications in ships and bridges, pipelines and chemical plants, automobiles, containers, and floor coatings etc [6-9].

1.2 EPOXY RESINS:

Epoxy resins are thermosetting matrix resins characterized by the epoxide, or oxirane, functionality. With the application of heat they cure chemically to a cross-linked, insoluble, infusible matrix resin. Like other thermosets they also form a network on curing with a variety of curing agents such as amines, anhydrides, thiols etc [10-16].

1.2.1. THE PROPERTIES OF EPOXY RESIN :

- ❖ Epoxy possesses excellent adhesion, mechanical properties and chemical resistance.

- ❖ Cure shrinkage is low when compared to other matrix resin.
- ❖ Epoxy possesses excellent processing characteristics[17-21].

1.2.2. ADVANTAGES OF EPOXY RESIN:

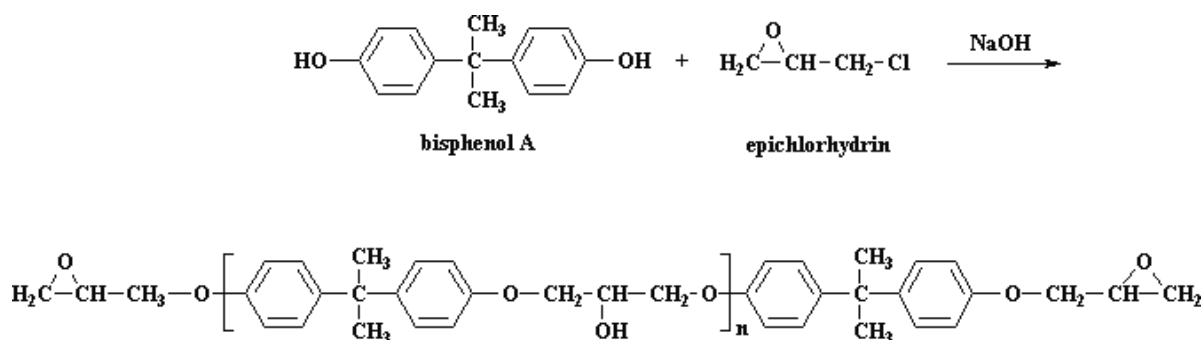
- ❖ Good shelf life.
- ❖ Ease of handling and processability,
- ❖ Low shrinkage on cure,
- ❖ Good adhesion to many substrates.

1.2.3. DISADVANTAGE OF EPOXY RESIN:

- ❖ Flammability and the limitation on their upper use temperature restrict their application[22-26].

1.3SYNTHESIS OF EPOXY RESINS

The epoxy was first developed commercial by reacting glycidyl ethers of bisphenol-A and epichlorohydrin (Bruins1968 and Potter 1970).They can be cured with wide range of curing agents. Curing is used to describe the process by which epoxy resins are transformed from lower molecular weight molecule into higher cross linking network and its achieved by the addition of curing agents[27-32].



1.4CURING AGENT :

The type of curing agents plays a major role in determining the properties of epoxy resin. It strongly influences the structure of the cross-linking epoxy phase, mechanical properties and morphology[33-36].

The most commonly used curing agent are aliphatic, primary and secondary amines, polyamidoamines and acid anhydride (Potter 1970 and Ashcroft 1993). Amine curing agents are most widely used because of the better understanding/control of epoxy-amine reactions.

The chemical structures of commonly used curing agents namely:

- ❖ 4,4' Diaminodiphenyl methane (DDM),
- ❖ 4,4' Diaminodiphenyl sulfone (DDS),
- ❖ Triethylene tetramine (TETA),

1.5 COMPOSITES

Composite materials may be defined as material composed of a reinforcement fiber and a resin matrix binder. This combination yields a unique class of material to be specifically tailored to the requirements. Because the properties of composites can be tailored to meet a broad spectrum of desired characteristics, they have found a wide variety of application in areas such as aerospace, automobiles, electronics, industrial, etc. On the basis of the nature of the matrices, composites can be classified into four major categories:[37-41]

1.5.1 Classification of composites

1. Polymer matrix composites(PMC)
2. Ceramic matrix composites(CMC)
3. Metal matrix composites (MMC)
4. Carbon matrix composites

Material within these categories are often called “**advanced** ” if they combine the properties of high strength, high stiffness, and low weight, corrosion resistance .

The reinforcement compatible with the matrix system may be in the form of filament(long fibers), short fibred, platelets, flakes, and particulates. Mostly preferred reinforcement are fibers or whiskers[42-45].

1.6 POLYMER MATRIX COMPOSITE (PMC) RESIN SYSTEM:

Polymer matrix composite continues to demonstrate a marked impact on the material world as evidenced by many recent advancement and exotic application due to PMC can be processed at a much lower temperature, compared to MMC and CMC. The composites possess many useful properties such as greater stiffness and strength, dimensional stability, excellent corrosion resistance, light weight and affordability.

Polymeric resin system used in manufacture advanced composites are thermoplastics and thermosetting. The composite industry is currently dominated by thermosetting resins namely epoxy, vinyl ester, unsaturated polyester, phenolic, polyimides, cyanate ester and so on. Of these, epoxide are the most commonly used in today's polymer matrix composites (PMS) industry. Epoxy resin based on diglycidyl ether of bisphenol-A have been used extensively as thermosetting matrices in the development of high-performance lightweight fiber reinforced composites.

1.7 NANOCOMPOSITES :

The oldest man-made composite is concrete, which is associated with a macro level reinforcement. The urge to improve the properties of composite materials, has prompted material scientists to investigate composites with lower and lower reinforcement size, leading to the development of nanocomposites (with nanometer scale reinforcements). They are relatively a new class of material, which exhibits ultrafine phase dimensions typically in the range (1-100) nm. Nanoreinforced composites or nanocomposites offer a great potential for novel properties because the distinct inorganic organic component properties can be combined in a single material with a uniformity of dispersion at the nano level.

Polymer composite especially polymer layered silicates nanocomposites, represents a radical alternative to (macroscopically) filled polymers. Because of their nanometer-size dispersion, the nanocomposites exhibits markedly improved properties when compare with pure polymer or conventional composites. These include increased strength, increases heat resistance and decreases flammability.

1.8 APPLICATION :.

The epoxy resins are widely used in **coating application**. The coatings industry is the biggest consumer of epoxy resins. The flammability of the epoxy resins is one of the major drawbacks in application where high flame retardancy is required. Flame retardant material can either be physically mixed with the epoxy base material (additive flame retardants) or chemically bonded to it (reactive flame retardants). The flame retardant coatings have many application which includes building construction, electronic application, and transportation.

1.8.1 Fire Retardant Epoxy Composites:

The second limitation of epoxy composites (polymer composites in general) is the poor fire resistance. These studies have shown that thermal softening of the polymer matrix and reinforcement, creep and decomposition of polymer matrix, deteriorate the tension properties, whereas matrix softening and delamination cracking are responsible for the reduction of compression properties. Hence, it is necessary to make the composite materials-based end products flame retardant to ensure reliability and human safety.

1.8.2 Flammability and Smoke Tests :

Three most commonly used flame tests, namely,

- ❖ Underwriters laboratory test (UL-94),
- ❖ Cone calorimetry ,
- ❖ Limiting Oxygen Index.

1.9 .METHODS FOR FLAME RETRADENT POLYMER :

The polymeric materials are commonly used in everyday life increasing fire hazards and flame-retardant are very often incorporated into them to limit their flammability. The flammability behavior of polymer is defined on spread rates(flame, pyrolysis, burn-outs), ignition characteristics and product distribution (in particular toxic species emission).

The approach to be considered to reduce the flammability of polymers :

- 1.To use inherently flame retarded
2. To chemically modify existing polymers
3. To incorporate flame retardants into polymers.

1.9.1DOPO as flame retardant:

- ❖ Phosphorus compounds become the main kind of flame retardants owing to their environment-friendly and high efficiency. Among them, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has received a notable attention worldwide because of its merits such as **good thermal stability, less toxicity, outstanding oxidation and water resistance**.
- ❖ The halogenated compounds are found to generate toxic gases and corrosive smoke as we find DOPO as an exception; hence they are the choice of halogen

free compounds. The modified epoxy resin system is done by copolymerizing Benzoquinone with DOPO, and the chemically modified (DOPO –BQ)resin has higher char yield and lower heat release rate.

1.9.2Hyper Branched Siloxane - (DOPO) as flame retardant:

- ❖ Silicones can be used as flame retardant agents by incorporating DOPO as a copolymers with silicone segments.
- ❖ Silicone is suitable modifier for epoxy resins, they provide not only significantly improved flame retardancy, but also much better integrated properties including thermal stability, toughness, stiffness, excellent moisture resistance, low surface energy and good hydrophobicity. The **(DOPO–PeHsi)** forms an insulating blanket of char layer which provide “shielding effect “to the resin.

3.1 MATERIALS AND METHODS

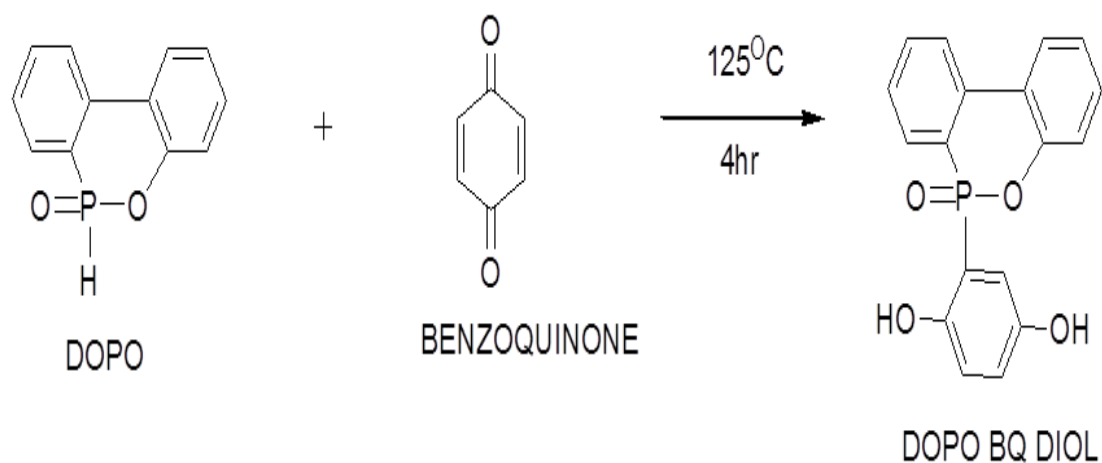
3.1.1 Materials

The organo-phosphorus compound (DOPO) was purchased from Tokyo chemical industry, Japan. Benzoquinone (BQ), Anthraquinone (AQ), Ethanol and Con. HCl was purchased from Avra synthesis pvt. Ltd, Ethanol was purchased from Changshu Yangyuan chemical, China. Azobisisobutyronitrile (AIBN) from Spectrochem Limited Mumbai. Vinyltriethoxy Silane (VTES) was purchased from Avra synthesis pvt. Ltd., Mumbai.

3.1.2 Synthesis of DOPO based Benzoquinone diol:

A 250 ml two-inlet flask was filled with 5g of (DOPO) and 20 mL of 2-ethoxyethanol. The mixture was heated to 90°C under a nitrogen atmosphere, and the stirring was continued until DOPO dissolved completely. Subsequently, 3.29g of Benzoquinone (BQ) was slowly added to this solution, and the temperature was then increased to 72°C, where it remained for 4.5 h. The mixture was filtered and further

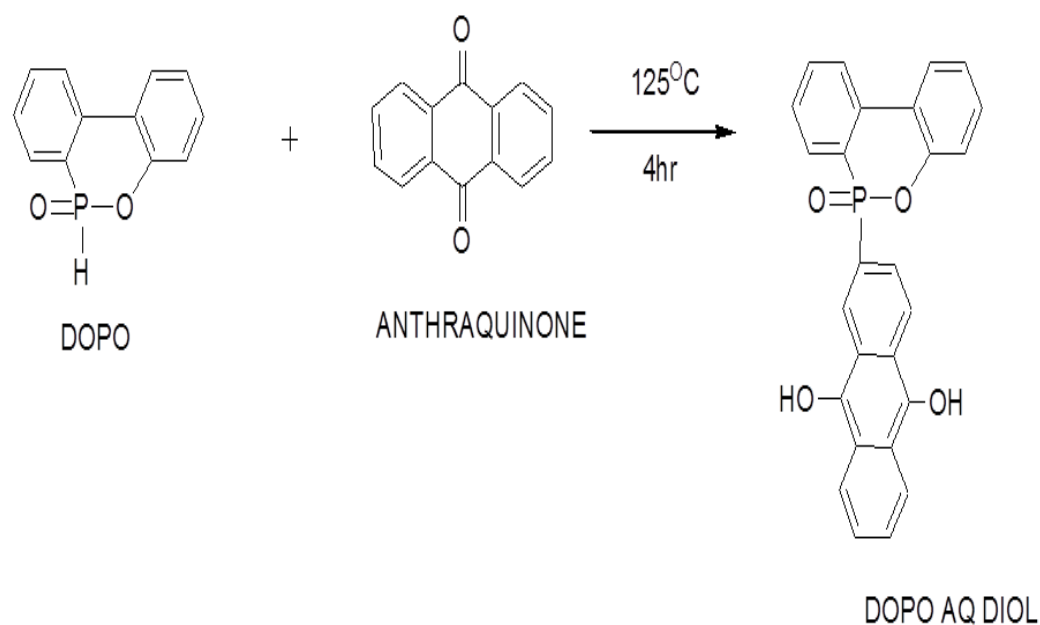
recrystallized from 2-ethoxyethanol to produce solid crystals of DOPO-Benzoquinonediol (DOPO-BQ).



Scheme 1: Synthesis of DOPO based benzoquinone diol (DOPO- BQ)

3.2 Synthesis of DOPO based Anthraquinone diol:

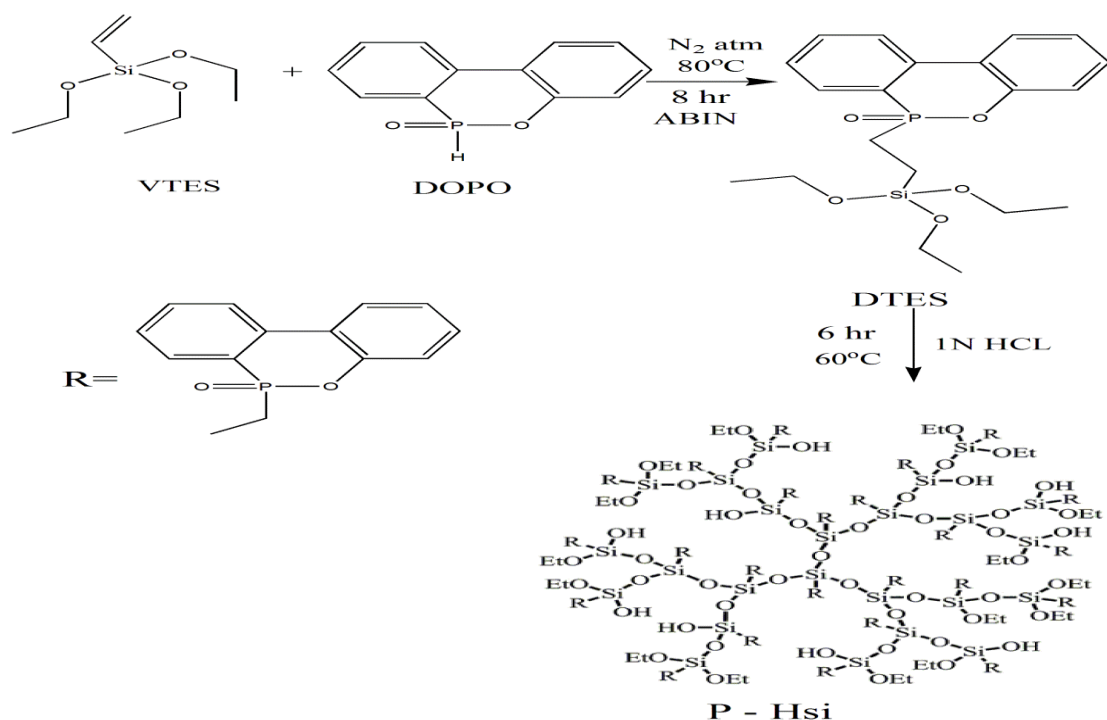
A 250 ml two-inlet flask was filled with 2g of (DOPO) and 20 mL of 2-ethanol. The mixture was heated to 90°C under a nitrogen atmosphere, and the stirring was continued until DOPO dissolved completely. Subsequently, 0.436g of anthraquinone (AQ) was slowly added to this solution, and the temperature was then increased to 125°C, where it remained for 4 h. The mixture was filtered and further recrystallized from ethanol to produce yellow powder of DOPO-Anthraquinonediol (DOPO-AQ).



Scheme 2: Synthesis of DOPO based Anthraquinone diol (DOPO- AQ)

3.3 Synthesis of hyper branched polysiloxane (PeHSi)-(DOPO):

A 250 ml two-inlet flask was filled with 1g of (DOPO) and VTES, AIBN and stirred under nitrogen atmosphere. The temperature was kept at 80°C for 8 h to obtain a light yellow liquid, coded as DTES under a nitrogen atmosphere, and the stirring was continued until DOPO dissolved completely. Then 12 g of distilled water was added to DTES, and HCL was slowly dropped to adjust the pH value of the solution between the range 2 and 3. After stayed at room temperature for 15 min, the solution was heated to 60°C and maintained for 2 h to get the crude product. The crude product was put into vacuum oven to dry off ethanol and then a transparent viscous liquid was obtained.



Scheme 3: Synthesis of hyper branched polysiloxane (PeHSi)-(DOPO)

RESULTS AND DISCUSSION

4.1 Structure of DOPO –BQ

In the FTIR spectrum the absorption peak at 3515 cm^{-1} indicates the formation of phenol, the distinctive peak at 2545 cm^{-1} for P-H stretch in DOPO disappears, which demonstrates the reaction of DOPO and Benzoquinone. The chemical structure of DOPO –AQ could be confirmed by the other adsorption peaks at 923 and 837 cm^{-1} for P-O-Ph. The peak at 1592 cm^{-1} for P-Ph and 1194 for P=O.

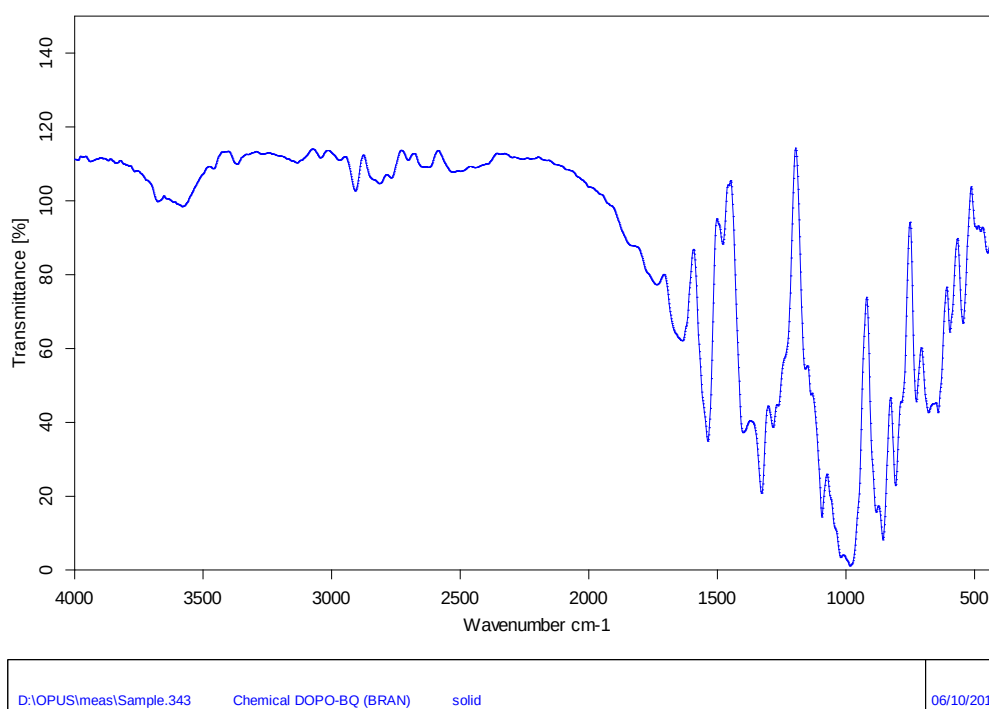


Fig.4.1: FTIR spectrum of DOPO –BQ

4.2 Structure of DOPO –AQ

In the FTIR spectrum of the absorption peak at 3495 cm^{-1} indicates the formation of Ph-OH, the distinctive peak at 2345 cm^{-1} for P-H stretch in DOPO disappears, which demonstrates the reaction of doPO and p-Anthraquinone. The chemical structure of DOPO –AQ could be conformed by the other adsorption peaks at 933 and 810 cm^{-1} for P-O-Ph. The peak at 1591 cm^{-1} for P-Ph, and 1165 cm^{-1} for P=O.

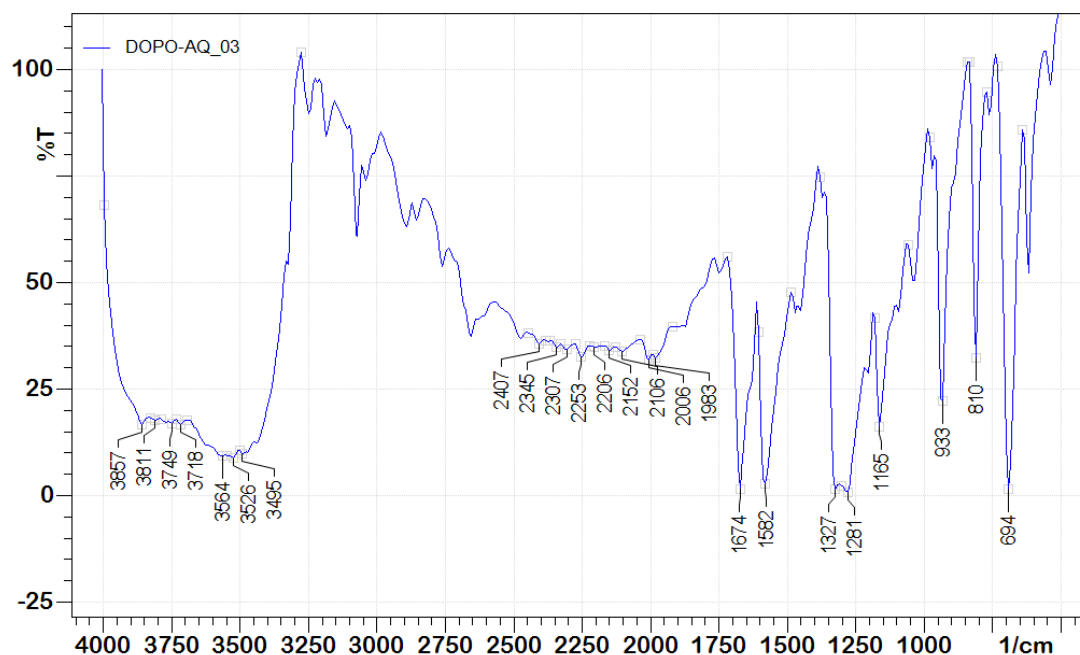


Fig.4.2: FTIR spectrum of DOPO –AQ

4.3 Structure Pe-HSi

In the FTIR spectrum of PeHSi the peak at 2436cm^{-1} attributing P-H groups of dopo completely disappears, the characteristic peaks assigning to phenyl 1474 cm^{-1} and C-H of 2924 cm^{-1} group appears indicating that DTES is the product of the reaction between DOPO and VTES. The characteristic peaks belonging to Si-O-Si groups in the range of 1180 to 1149 cm^{-1} , while the broad peak centered at 3441cm^{-1} representing Si-OH groups also can be observed, small and wide peak appears in the range from 1185 cm^{-1} to 1258 cm^{-1} . Obviously, this results from the overlay of the stretching vibration of P=O.

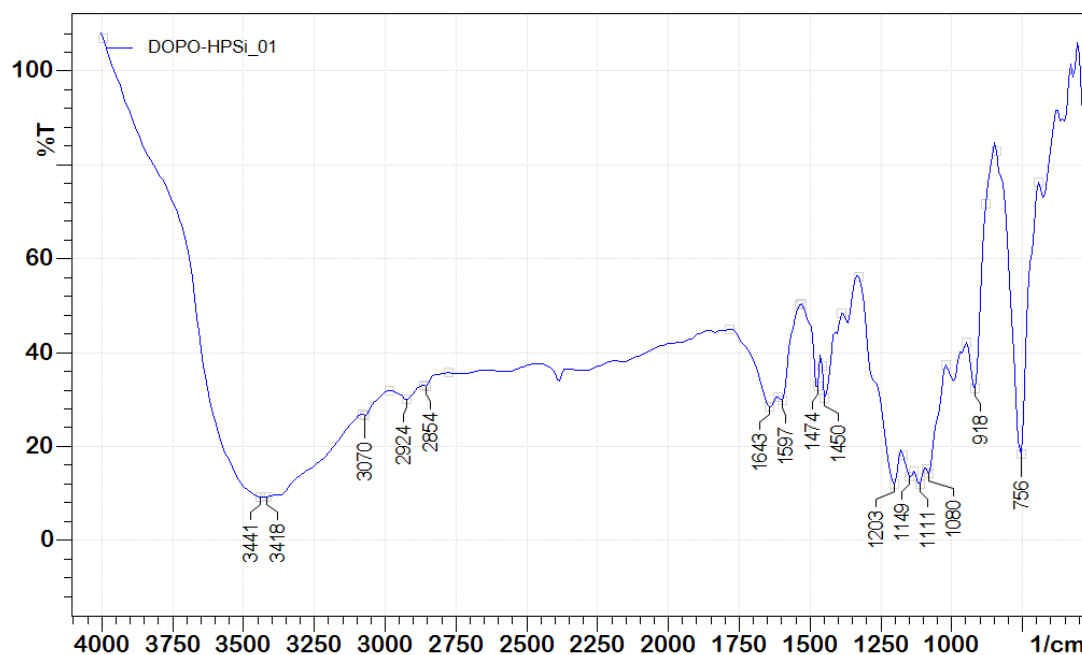


Fig.4.3: FTIR spectrum of Pe-HSi

5.1 CONCLUSION

The present work deals with the development and characterization of DOPO based bezoquinone (DOPO-BQ) diol and DOPO based Anthraquinone diol (DOPO-AQ) and phosphorous containing hyperbranch polysiloxane (P-HSi) was synthesized and characterized.

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