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Synthesis and comparative study of vinyl ester resin prepared by using methyl methacrylate and acrylic acid

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ABSTRACT

Epoxy resins based on β -Naphthol tri hydroxy phenols have been prepared than vinyl ester resin with acrylic acid or MMA have been prepared and characterized. Thus by two methods vinyl ester resin was formed. Fourier transform infra-red (FT-IR) analysis was used to see the structural changes during the formation of vinyl ester resin (VER). The unreinforced cured resins were subjected to thermogravimetric analysis (TGA).

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KEYWORDS

Vinyl ester resins (VER);
Characterization;
Methyl methacrylate
(MMA);
Thermo gravimetric
analysis (TGA);
Fourier transform
infra-red (FT-IR).

INTRODUCTION

Vinyl ester resins are addition products of various epoxide resins and unsaturated monocarboxylic acids (acrylic, crotonic or cyanoacrylate)^[1] They have terminal reactive double bonds derived from the carboxylic acid used. Vinyl ester resin are used to fabricate a variety of reinforced structures including pipes, tanks, scrubbers and ducts^[2-9]. They are prime candidates for use in composites for transportation and/or infrastructure. Such applications include fabricating of part for automobiles and other surface transportation vehicles fascia for building and reinforcement for bridges etc. The main feature of the vinyl ester resins are: resistance to water and chemical compounds, higher thermal and electrical stability, reduced content of the volatile materials evolved during manufacture, mechanical resistance and decreased contraction to the strength tensing^[10]. In addition to these applications, vinyl esters are also being used in coating,

adhesives, molding compounds, structural laminates, electrical and military/aerospace applications.

The properties of the vinyl ester resins are dependent on their chemical nature, molecular mass and cross-linking degree. The physical properties of the vinyl ester networks are in general, superior to the unsaturated polyesters, particularly corrosion resistance. This can be at least partially attributed to the fact that the ends of the chain only while the unsaturated polyester resins have the reactive double bonds distributed throughout the chains.

In this paper, we report the synthesis and characterization of vinyl ester resin obtained as a result of the reaction between epoxy resin and acrylic acid/methyl methacrylate (MMA).

METHODS AND MATERIALS

Materials

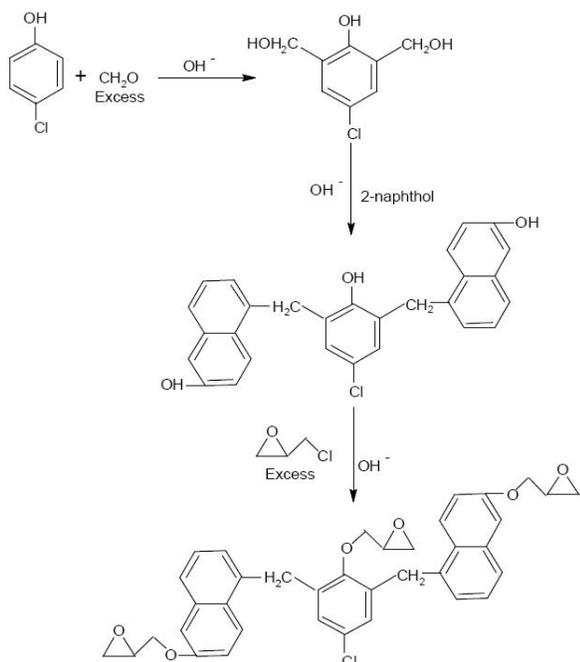
All the chemicals used in the present work were of

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Analytical grade or purified by literature method.

Synthesis of epoxy resin

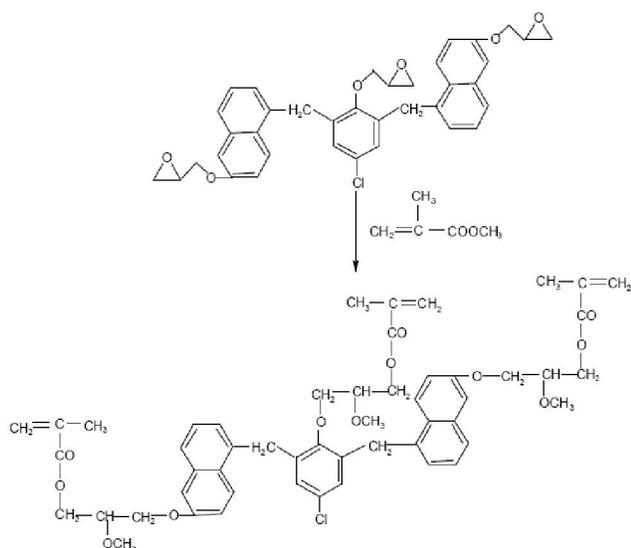
p-Chloro phenol and formaldehyde were taken in 1:2 ratios and refluxed in basic medium of NaOH for 45 minutes to form dimethylol resin. This resin was condensed with 2-Naphthol for 18 hours. Epoxidation of phenolic resin with epichlorohydrin is done to form triglycidyl ether in basic medium for 10 hours. The novel epoxy resin is formed.



Synthesis of vinyl ester resin

(1) By reacting with MMA

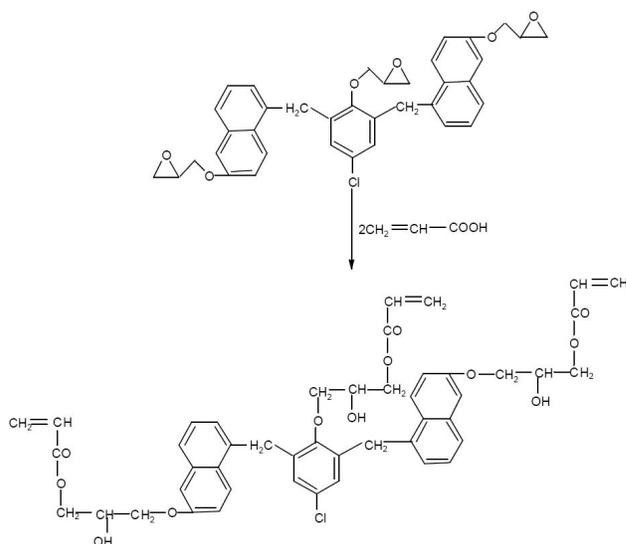
The synthesized epoxy resin was refluxed with



MMA which were taken in 1:2 ratios for 6-7 hours at 100°C. To this 0.1 mole of hydroquinone was added as a catalyst and pyridine was used as an inhibitor. The synthesized vinyl ester resin was characterized duly. It was in the form of pasty mass.

(2) By reacting with acrylic acid

Synthesized epoxy resin and acrylic acid in 1:2 ratio were charged in three necked flask equipped with a mechanical stirrer for 6-7 hours at 100°C. Hydroquinone was used as a catalyst. Few drops of pyridine were used as an inhibitor. The resin was then discharged to give vinyl ester resin. It was in the form of pasty mass.



MEASUREMENT

The elemental analyses of resins were carried out by means of Carlo Earba Model NA 500 series analyzer (Italy). Fourier transform infrared (FTIR) spectra were obtained using KBr pellet on Perkin Elmer (Model 2000) Spectrometer Thermogravimetric analysis (TGA) of resins have been carried out using using Metler Torido AG 2007 system at heating rate of 10°C/minute. The sample weight for this investigation used was in the range of 4-5 mg.

RESULTS AND DISCUSSION

The elemental analysis data are consistent with the suggested chemical structure of the resins. The results are summarizes in TABLE 1

TABLE 1 : Elemental analysis

| Resin | Resin code | C% | | H% | |
|-------------------|------------|----------|------------|----------|------------|
| | | Observed | Calculated | Observed | Calculated |
| Epoxy resin | E-3 | 69.03 | 72.96 | 5.68 | 5.42 |
| Vinyl ester resin | VE-3(a) | 65.43 | 68.68 | 6.98 | 6.27 |
| Vinyl ester resin | VE-3(b) | 65.42 | 66.94 | 5.02 | 5.45 |

Vinyl ester resin of chloro phenol with MMA (VE-3 (a)), Vinyl ester resin of chloro phenol with acrylic acid (VE-3 (b)). Epoxy resin of chloro phenol (E-3)

FT-IR spectra of epoxy resin

FT-IR spectra of epoxy resin is shown in figure 1. Band at 905.07 cm^{-1} in epoxy resin was due to epoxy group and absence of band near $3400\text{--}3600\text{ cm}^{-1}$ which is of hydroxyl group confirms the formation of epoxy resin. The absorption band near 1439.06 , 1515.29 ,

1583.20 cm^{-1} might be due to aromatic C=C bond of phenolic ring. Peak at 743.54 and 850.26 cm^{-1} were due to ortho and para substitution of phenolic ring. Peak at 1354.50 cm^{-1} and 2918.65 cm^{-1} was due to bending and stretching of CH_2 group. Peak at 3195.18 cm^{-1} was due to aromatic CH of phenolic ring.

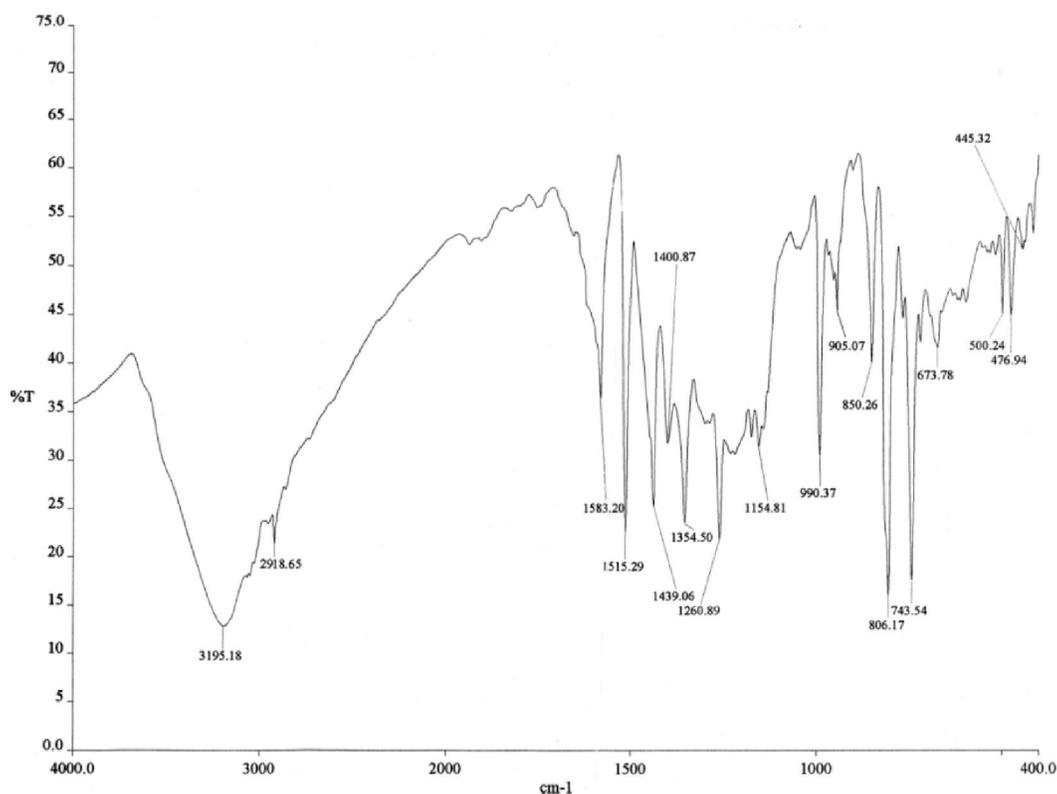


Figure 1

FT-IR spectra of vinyl ester resin

FT-IR spectrum of synthesized vinyl ester resins are shown in figure 2 and 3. The preparation of resins were confirmed with the IR spectrum study. Band at 1718.46 and 1722.24 cm^{-1} in vinyl ester spectrum is due to carbonyl group of the ester. Due to the stretching and bending of vinyl groups the absorption band at 1627.61 , 1629.74 cm^{-1} , 1026.23 and 964.34 cm^{-1} were present. The lack of ether absorption band at

1120 cm^{-1} also confirms the completion of epoxy esterification reaction. The peaks of epoxide groups (6066 , 4530 , 917 cm^{-1}) were no longer visible and methacrylate group peak at 958.56 cm^{-1} was present. Due to acrylol double bond peak at 1598.85 cm^{-1} was present. The results indicate that the epoxide group reacted to near completion with MMA and acrylic acid. The peak at 678.90 , 660.83 cm^{-1} were due to chloro group at para position.

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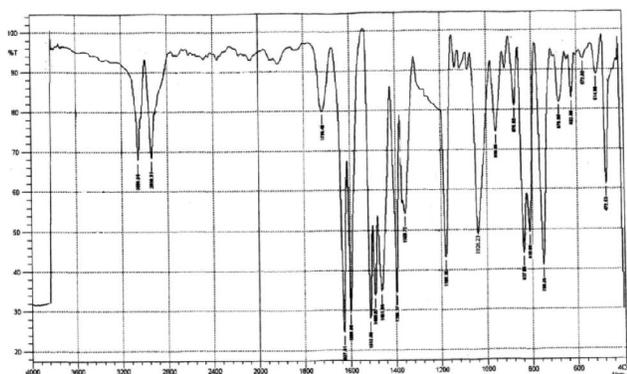


Figure 2

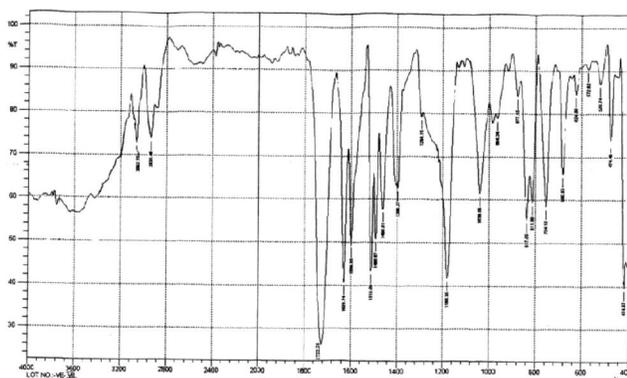


Figure 3

Thermogravimetric analysis of resins

Thermogravimetric Analysis gives the overall picture of the polymer degradation pattern, stability etc. TG thermograms are shown in figure 4 and 5. Both the resin shows two step degradation patterns. First step of degradation is fast which is attributed to loss of side groups (vinyl, methoxy, carbonyl, ester) and second step of decomposition is slow step which may be due to main chain breakdown and increase in extent of crosslinking.

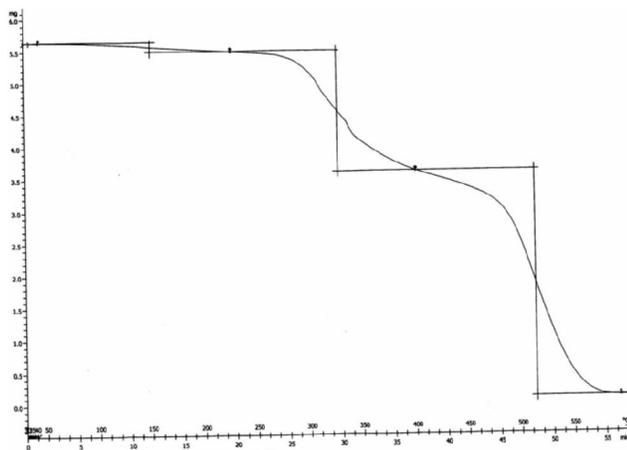


Figure 4

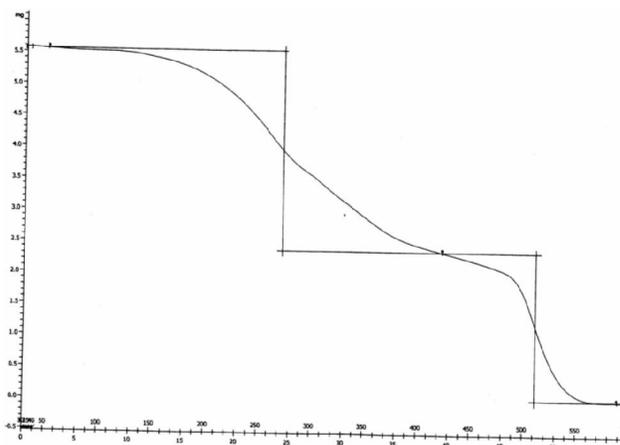


Figure 5

The initial decomposition temperature (T_i), maximum weight loss temperature (T_{max}) and final decomposition temperature (T_f) are given in TABLE 2 and 3 for step-1 and step-2 respectively.

TABLE 2 : Thermal behaviour of resins

| Vinyl ester code | Initial decomposition temperature (T_i) | Maximum weight loss temperature (T_{max}) | Final decomposition temperature (T_f) |
|------------------|---|---|---|
| VE-3(a) | 190 | 260 | 400 |
| VE-3(b) | 150 | 240 | 420 |

TABLE 3

| Vinyl ester code | Initial decomposition temperature (T_i) | Maximum weight loss temperature (T_{max}) | Final decomposition temperature (T_f) |
|------------------|---|---|---|
| VE-3(a) | 400 | 470 | 600 |
| VE-3(b) | 420 | 480 | 600 |

CONCLUSION

Epoxy based vinyl ester resins were synthesized by reacting with MMA and acrylic acid. The FT-IR spectrum confirms the structure of the resins. The results of elemental analysis are also consistent with the suggested chemical structure of the resins. The resins show thermal stability property. The thermogravimetric analysis suggested that the vinyl ester resin prepared with MMA was more stable as compared to the resin prepared with acrylic acid. Due to high molecular weight of VE-3(a) it was more stable as compare to VE-3(b).

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