

Synthesis & Characterization of Vinyl Ester Resins of p-Cresol and Tertiary Butyl Phenol

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Abstract

The vinyl ester resins were prepared by the reaction between synthesized epoxy resin and methyl methacrylate (MMA). The paper presents the synthesis and characterization of some vinyl ester resins. The resins were characterized by their, elemental analysis and solubility. Fourier transform infra-red spectroscopic (FT-IR) analysis was used to confirm the structural changes on the synthesis of the vinyl ester resin (VER). The thermal stability of the resins was investigated by thermo gravimetric analysis (TGA).

Keywords: Vinyl ester resins (VER), Methyl methacrylate (MMA), Thermogravimetric analysis (TGA), Characterization, Fourier transform infra-red spectroscopic (FT-IR)

Introduction

Vinyl ester resins are difunctional methacrylated epoxy polyesters i.e. they consist of a polymer backbone with an acrylate or methacrylate termination [1, 2]. Vinyl ester resins are of major interest, with various applications, such as composites for manufacturing of pipes, tanks, filter devices, sewerage pipelines, dental materials, photo-crosslinking inks etc [3, 4]. Vinyl ester resins provide greater toughness, heat distortion temperature and corrosion resistance compared to conventional unsaturated polyesters [5]. These resins also find a variety of applications in optical fiber coating, topcoats for metal containers, UV curing inks, as well as in printed circuit boards because of their ability to constitute photocrosslinkable systems [6]. Vinyl ester resins are also found applicability in special domains, such as aeronautic, naval and auto vehicle, constructions towards biomedical science [7] and in the construction of waste incineration gas cleaning units. [8]

Bowen *et al.* also prepared vinyl ester resin by the reaction of glycidyl methacrylate with a multifunctional phenol. D.J. Najvar [9] and A.R. Siebert [10] synthesized vinyl ester resins by taking excess of the selected epoxy resin with selected difunctional carboxyl-terminated reactive liquid polymers and an unsaturated mono-carboxylic acid.

In the present paper we report vinyl ester resin was synthesized using epoxy resin and MMA catalyzed by hydroquinone and its characterization. In this reaction pyridine is used as an inhibitor

Methods and Materials

All the chemicals used in the present work were of analytic grade or purified by literature method.

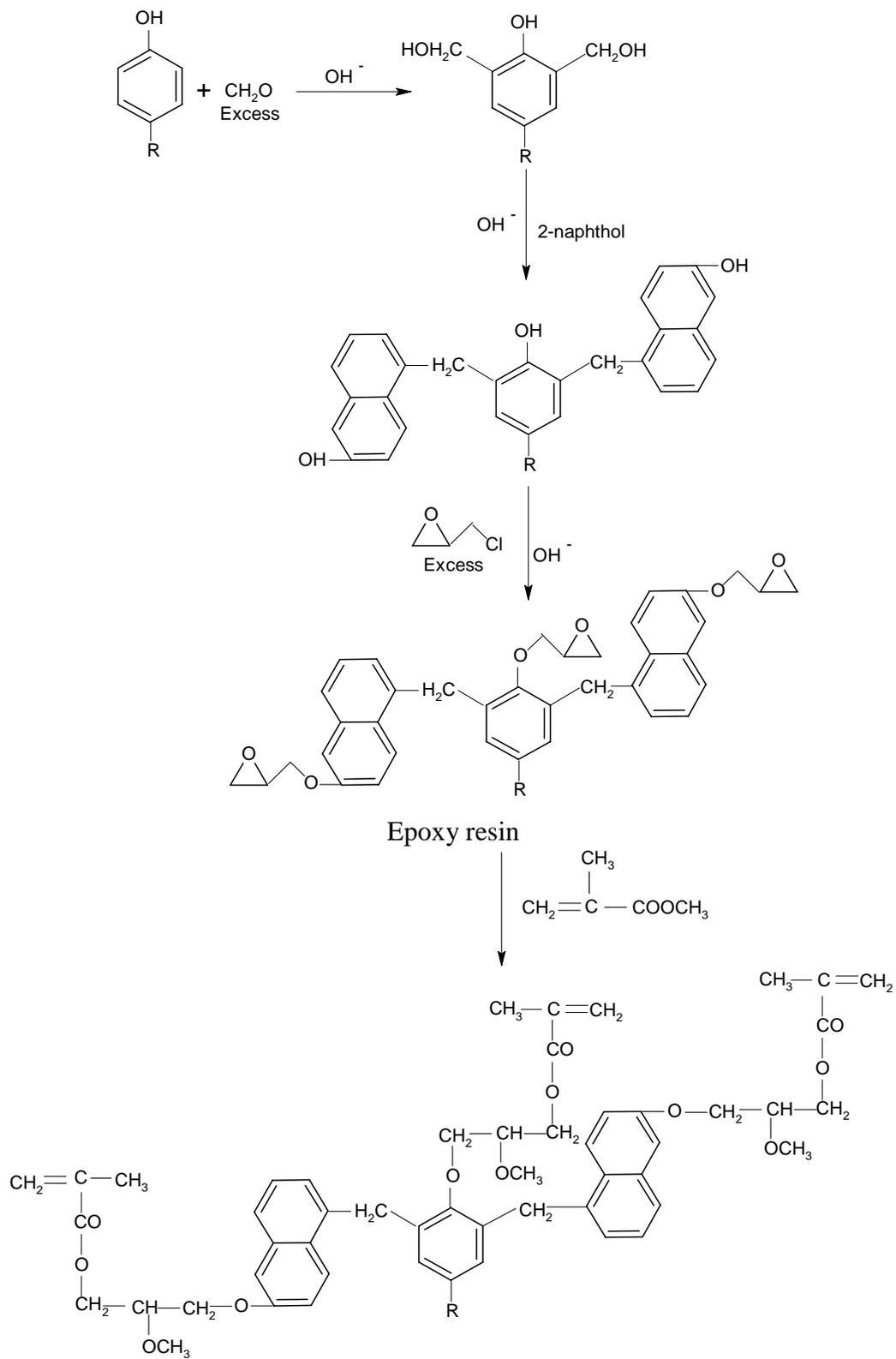
Experimental

Synthesis of Epoxy Resin

p-Cresol/tert.-butyl phenol and formaldehyde in 1:2 ratios were charged in three necked flask equipped with a mechanical stirrer. It was then refluxed in basic medium using NaOH for 45 minutes to form dimethylol resin. Condensation of this resin with 2-naphthol is carried out for 18 hours to form phenol resin. Epoxidation of phenolic resin with epichlorohydrin is done to form triglycidyl ether in basic medium for 10 hour.

Synthesis of Vinyl Ester Resins

Synthesized epoxy resins (33gm) and MMA (10.6gm) in 1:2 ratio were charged in three necked flask equipped with a mechanical stirrer for 6-7 hours at 100⁰C. To this 0.1 mole of hydroquinone was added as a catalyst. Few drops of pyridine were used as an inhibitor. The resins were then discharged to give vinyl ester resins. These were in the form of pasty mass.



Characterization

Solubility test was carried out by taking 0.05 gm of the resins and treating it with 2 ml of the solvent at the room temperature and shaking well. The C, H, contents were estimated by means of Carlo Erba Model NA 500 Series Analyzer (Italy). The presence of unsaturation was predicted by Bromate –Bromide titration method.

Fourier transform infrared spectra (FT-IR) were obtained using KBr pellet on Perkin Elmer (Model 2000) spectrometer. A plot between weight loss and temperature was recorded by thermo gravimetric analysis (TGA) using Metler Torido AG 2007 system at heating rate of 10⁰C/minute. The sample for this investigation was used in the range of 5-7 mg.

Results and Discussion

The solubility of resins in number of polar and non polar solvents at 30⁰C were summarized in table 1.1.

Table 1.1: Solubility behavior of resins in polar and non-polar solvents at 30⁰C

Solvent	VE-1	VE-2
Ethanol	S	S
Methanol	S	S
CH ₂ Cl ₂	S	S
Chloroform	P.S	P.S
Carbon tetra chloride	P.S	P.S
Ethyl acetate	P.S	S
Methyl acetate	P.S	S
THF	S	S
DMF	S	S
Acetone	S	S
Benzene	I.S	I.S

S=Soluble

P.S=partially soluble

I.S=Insoluble

VE-1 (Vinyl ester resin of p-cresol),

VE-2 (Vinyl ester resin of tert. butyl phenol),

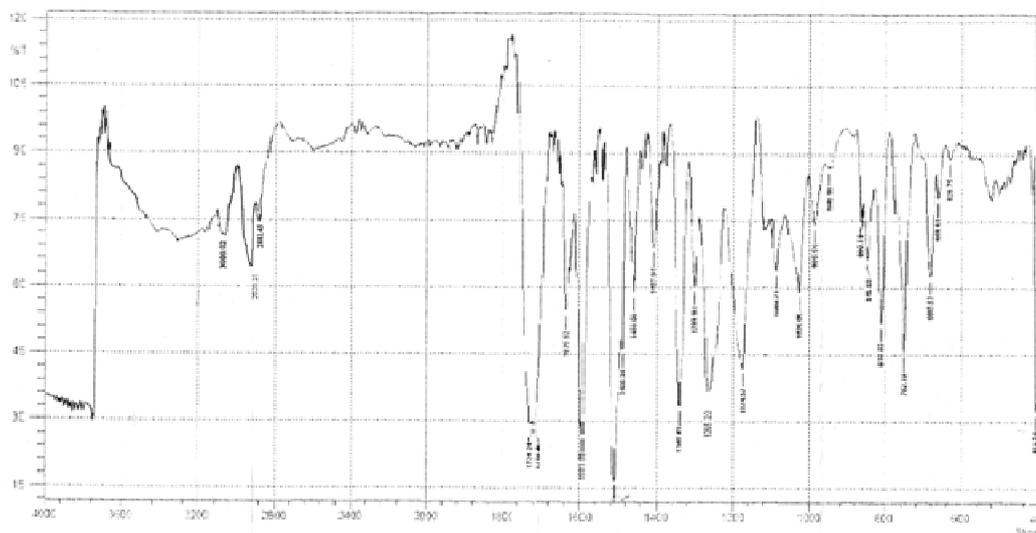
The elemental analysis data are consistent with the suggested chemical formulae of the resins. The results are reported in table 1.2

Table 1.2: Elemental analysis

Resin	Resin code	C %		H%	
		Observed	Calculated	Observed	Calculated
Vinyl ester resin	VE-1	69.65	71.62	6.05	6.75
	VE-2	70.08	72.25	6.96	7.096

FT-IR Spectra of vinyl ester resins

FT-IR spectrum of synthesized vinyl ester resins are shown in figure 1 and 2. The preparation of resins was confirmed with the IR spectrum study. Band at 1724.24cm^{-1} and 1716.53cm^{-1} in vinyl ester spectrum is due to carbonyl group of the ester. The absorption bands due to stretching and bending vibration of vinyl groups were present at 1636.82 , 1631.00cm^{-1} and 1026.05 , 1037.63cm^{-1} respectively which confirms the formation of vinyl. Furthermore lack of ether adsorption band at 1120cm^{-1} also confirms the completion of epoxy esterification reaction. The peaks representing the epoxide groups (6066cm^{-1} , 4530cm^{-1} , 917cm^{-1}) were no longer visible after reaction and methacrylate groups (985.58cm^{-1} , 985.00cm^{-1}) were present in the resins. The results indicate that the epoxide groups reacted to near completion with MMA. The peak at 2938.31cm^{-1} and 1394.44cm^{-1} was due to methyl and t-butyl group at para position respectively.

**Figure 1**

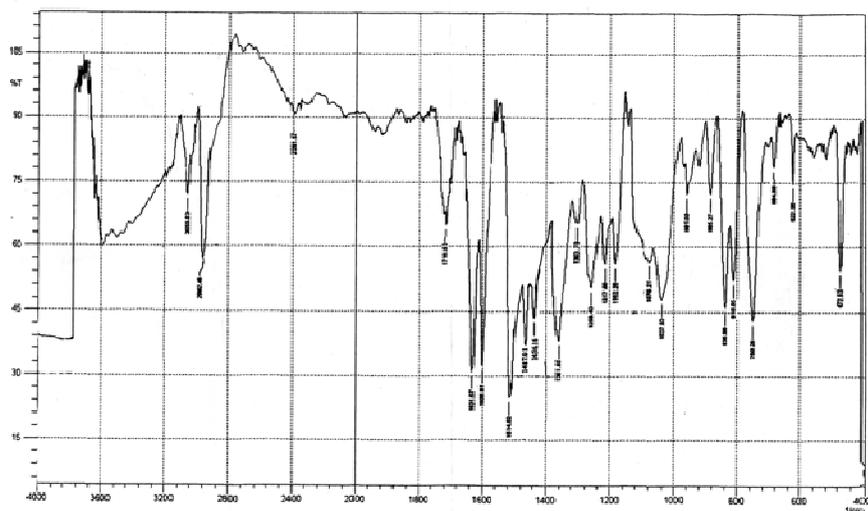


Figure 2

Thermogravimetric Analysis of resins

Thermogravimetric Analysis gives the overall picture of the polymer degradation pattern, stability etc. Decomposition kinetics can be calculated and processability can be established. TG thermograms are shown in figure 3 and 4. Both resins undergo two step degradation which is tabulated in table 1.3. First step degradation is rapid stage of degradation which is attributed to loss of side groups (carbonyl, methoxy, vinyl, ester) and second step decomposition step decomposition is slow stage of decomposition which may be due to main chain scission and increase in extent of crosslinking.

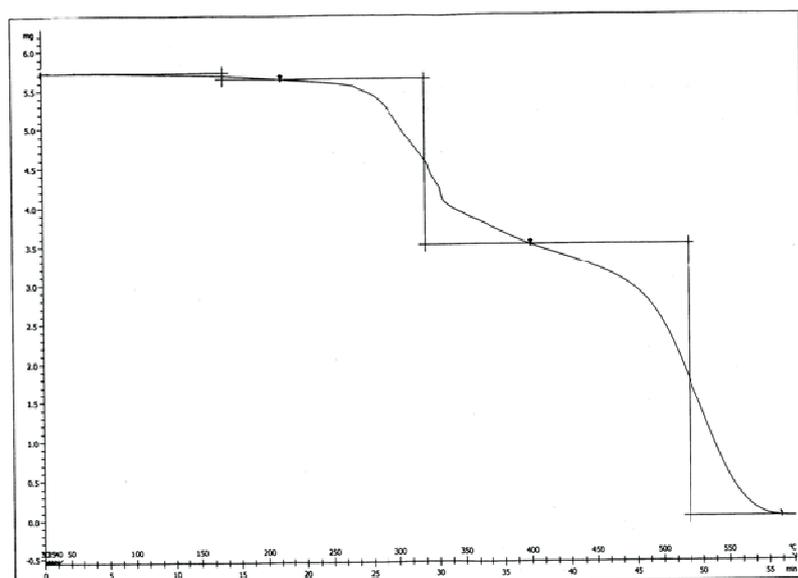


Figure-3

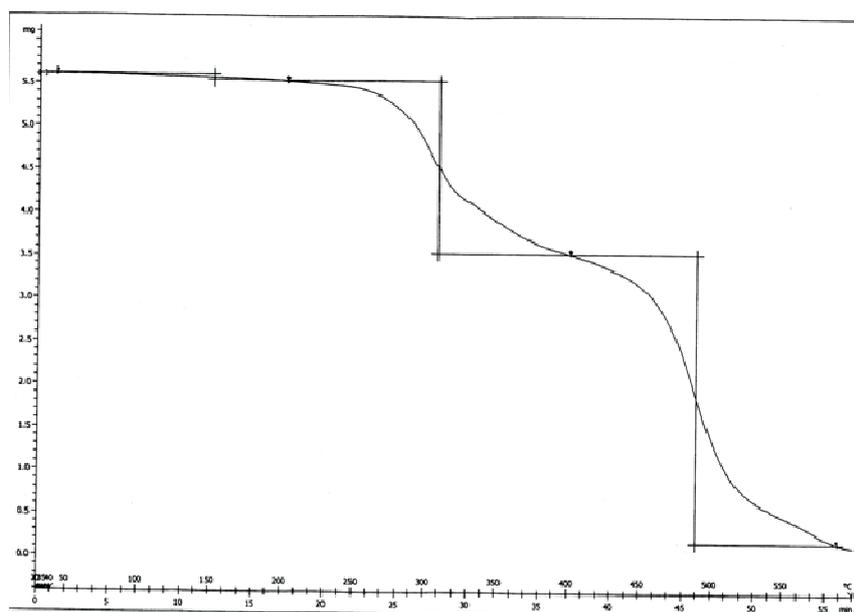


Figure-4

Table 1.3: Thermal behaviors of resins

Resin Code	Degradation step-1 ($^{\circ}\text{C}$)	Degradation step-2 ($^{\circ}\text{C}$)	Residue of resins at 600°C
VE-1	210-410	410-600	8.31%
VE-2	200-400	400-600	6.37%

Conclusion

All the resins showed good solubility in many polar solvents. The FT-IR spectrum confirms the structure of resins. The elemental analysis data are consistent with the suggested chemical formulae of the resins. The resins show thermal stability property. The thermogravimetric analysis suggests that the initial decomposition temperature of VE-1 (210) was found higher than VE-2 (200). This is due to steric hindrance of the tert. butyl (bulky group), thus it degrades easily as compared to the methyl group. Thus VE-1 was more thermally stable.

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