

## Curing and Decomposition Behaviour of Cresol Novolac Based Vinyl Ester Resin

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Vinyl ester resins were prepared from o, m, p-cresol epoxy novolac resin and methacrylic acid in the presence of triphenyl phosphine as catalyst and hydroquinone as polymerization inhibitor. The vinyl ester resin samples having acid value of ~ 7 mg of KOH/g of solid thus obtained were characterized by Fourier transform infra red spectroscopy (FT-IR) and Proton nuclear magnetic spectroscopy (<sup>1</sup>H-NMR). Samples were prepared at 30 °C from o-cresol novolac epoxy vinyl ester resin using styrene and methyl-methacrylate, respectively as reactive diluents. The curing behaviour of these samples in the presence of benzoyl peroxide (2 phr) as initiator was studied using Differential Scanning Calorimetry (DSC). The sample prepared from o-cresol epoxy novolac was found to be the more reactive than the sample prepared from m and p-cresol epoxy novolac during curing in the presence of styrene as reactive diluent. These samples were cured isothermally at 90 ± 2 °C for 2 hours. The decomposition behaviour of all these samples was studied by thermo gravimetric analysis (TGA) at a heating rate of 10 °C min<sup>-1</sup>. It was observed that vinyl ester resin based on o-cresol novolac epoxy containing styrene gave a more thermally stable product than the methyl methacrylate probably due to presence of aromatic ring.

### 1. Introduction

Vinyl ester (VE) resins are widely used thermosetting resins because of their low cost, excellent chemical and corrosion resistance, outstanding heat performance and favourable mechanical properties. Their advantage of being processable over a wide range of temperature is of vital importance for many end uses, such as in solvent storage tanks, sewer pipes, building and construction, coating, automobile structural parts, swimming pools, marine composites [Brown and Mathys., 1997]. These are the addition products of epoxy resins and α-β unsaturated carboxylic acids [Launikitis, 1982]. Vinyl ester resins in the neat or undiluted form vary from semisolid to solid. The viscosity of neat resin is considerably high (10<sup>5</sup> cPs) and therefore utilizes reactive or nonreactive diluents to provide workable viscosity levels and enhanced reactivity. These diluents also control the crosslink density and affect strength, percent elongation, hardness, chemical resistance, scratch resistance and surface finish. The curing and decomposition behaviour of vinyl ester resin containing methyl, ethyl, and butyl acrylate as reactive diluents was investigated by Gaur and Rai, 1993. It has been reported that vinyl ester resin sample containing ethyl acrylate showed lower activation energy for the curing reaction and better thermal stability and higher activation energy for the decomposition reaction. Thermal studies on styrenated vinyl ester resins by Varma et al., 1985 and Bhatnagar et al., 1989, showed that α-methyl styrene prolonged the cure time but did not adversely affect the physical properties. However, no difference in thermal stability was observed by replacement of styrene with α-methyl styrene.

Most of the studies related to thermal behaviour of such resins have been reported either on bisphenol-A epoxy based vinyl ester resin or on phenol formaldehyde novolac epoxy based vinyl ester resins. In the present communication, we have synthesised a new series of vinyl ester resins based on o, m, and p – cresols novolac epoxy resins and further explored and studied the thermal behaviour of these resins in the presence of styrene and methyl methacrylate as reactive diluents.

## 2. Experimental

### 2.1 Materials

O-Cresol, m-cresol, p-cresol (CDH) and formaldehyde [37-41 % solution, Fisher scientific] were used for the preparation of novolacs. Epichlorohydrin L.R. grade (Lobachemie) and sodium hydroxide pellets (Merck) were used for preparation of epoxy novolacs. Methacrylic acid (Lobachemie) and triphenylphosphine (Lobachemie) were used for synthesis of vinyl ester resins. Styrene (ACROS ORGANICS), methyl acrylate and methyl methacrylate (CDH) were used as reactive diluents in the present study.

### 2.2 Synthesis of ortho/meta/para-cresol formaldehyde novolac resin (OCN/MCN/PCN):

Cresol and formaldehyde in the molar ratio of 1: 0.7 were used for the preparation of novolac resins. Weighed amount of cresol (108 g) was dissolved in 11 mL of water and its pH was adjusted to 1.5 with p-toluenesulphonic acid and was charged into a 500 mL capacity, three necked flask equipped with mechanical stirrer, a mercury thermometer and a Liebig condenser. The solution was heated to 80 °C with constant stirring and formaldehyde solution (55.3 mL) was added in a drop wise manner over a period of 3 hours. 40 mL of 10 % sodium bicarbonate was added to neutralize the acid and arrest the reaction. 3-4 washings with warm water were done to neutralize the pH. The resin was finally dried at 80 °C under reduced pressure (35 ± 5 mm Hg).

### 2.3 Synthesis of Epoxy novolac from ortho/meta/para-cresol formaldehyde novolac resin (EOCN/EMCN/EPCN)

Epoxy novolac resins were prepared by reacting the above prepared novolac resin with epichlorohydrin in molar ratio 1:5. Sodium hydroxide (40 % w/w) was used as a catalyst, in molar ratio of 0.2: 1.0 to that of epichlorohydrin. Epoxidation was carried out at temperature 112 ± 1 °C for three and half hours. The excess of epichlorohydrin was distilled off under reduce pressure. The mixture obtained was cooled and dissolved in toluene and filtered using Whatman filter paper no. 42 to remove the salts. Toluene was distilled and product obtained was dried at 60 °C under vacuum for 48 hours. Epoxide equivalent weight for these epoxy resins determined by using pyridinium chloride method [Knoll et al.,1958] were found to be 200.3, 263.15, 233.1 for EOCN, EMCN and EPCN respectively.

### 2.4 Synthesis of vinyl ester resin from ortho/meta/para-cresol epoxy novolac (VEOCN/VEMCN/VEPCN):

Vinyl ester resins were prepared using 1:0.9 molar ratios of ortho/meta/para-cresol epoxy novolac resin and methacrylic acid in the presence of triphenyl phosphine (1 phr by weight of epoxy resin) and hydroquinone (200 ppm) at 85 ± 1 °C. The esterification reaction was carried out for three and a half hours to obtain a product with acid value of ~7 mg of KOH/gm solids determined according to ASTM D 1636. The VER samples were stored in refrigerator at 10 °C.

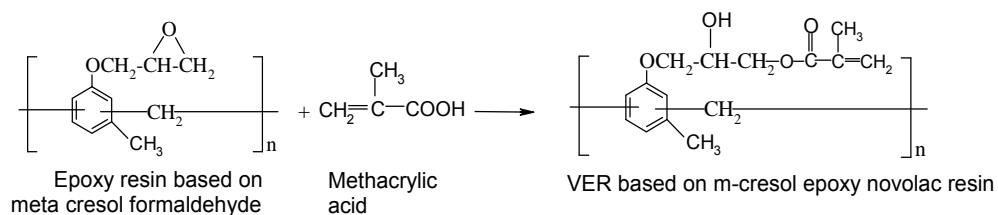


Figure 1: Scheme for reaction of epoxy novolac with methacrylic acid catalysed with triphenylphosphine.

## 3. Characterization

### 3.1 Structural characterization

The structural characterization of o-cresol formaldehyde novolac (OCN), m-cresol formaldehyde novolac (MCN), p-cresol formaldehyde novolac (PCN), o-cresol epoxy novolac resin (EOCN), m-cresol epoxy novolac resin (EMCN), p-cresol epoxy novolac resin (EPCN) and vinyl ester resins based on these respective o, m, p-cresol epoxy novolac resins was done using FTIR and <sup>1</sup>H-NMR spectroscopy. The FTIR spectra of the samples were recorded by dissolving in chloroform and subsequent evaporation of solvent on KBr disc. Perkin Elmer FTIR Spectrometer was used for this purpose. The <sup>1</sup>H-NMR spectra of these

samples were recorded using Bruker Avance II 400 NMR spectrometer,  $\text{CDCl}_3$  as solvent and tetramethylsilane as an internal standard.

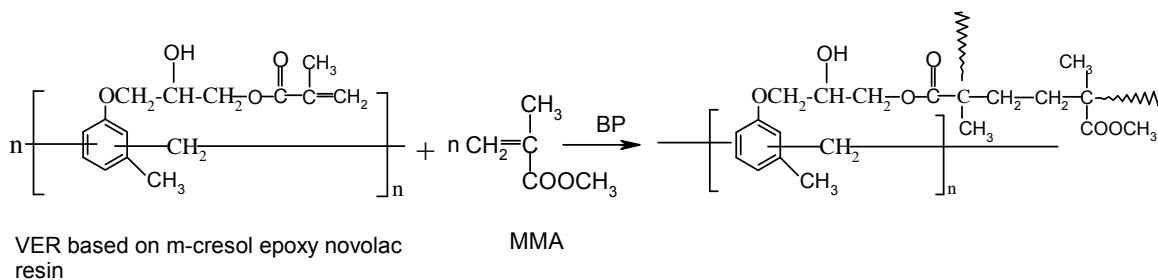


Figure 2: Scheme for curing of Vinyl ester resin with MMA as reactive diluent and benzoyl peroxide as free radical initiator.

### 3.2 Curing and Decomposition behaviour of Vinyl ester resins

The samples for curing and decomposition behaviour were prepared by mixing 10/4/0.2 (w/w) of vinyl ester resin, reactive diluents—styrene, methyl methacrylate and free radical initiator-benzoyl peroxide, respectively, in small glass vial and stirred vigorously with a glass rod at  $30^\circ\text{C}$  until the mixtures became homogeneous in nature. DSC scans under dynamic conditions were obtained with program rate of  $10^\circ\text{C min}^{-1}$  from  $35^\circ\text{C}$  to the temperature at which the exothermic reactions were completed.

Thermal stability of the samples cured isothermally at  $90 \pm 2^\circ\text{C}$  in hot air oven was evaluated by thermogravimetry. TG/DTG traces in nitrogen atmosphere (flow rate =  $200\text{ mLmin}^{-1}$ ). EXSTAR TG/DTG 6300 was used to record TG/DTG traces at heating rate of  $10^\circ\text{Cmin}^{-1}$  with sample size  $11 \pm 5\text{ mg}$ . The relative thermal stability of the resin was quantitatively estimated by comparing the temperature for a particular degree of weight loss.

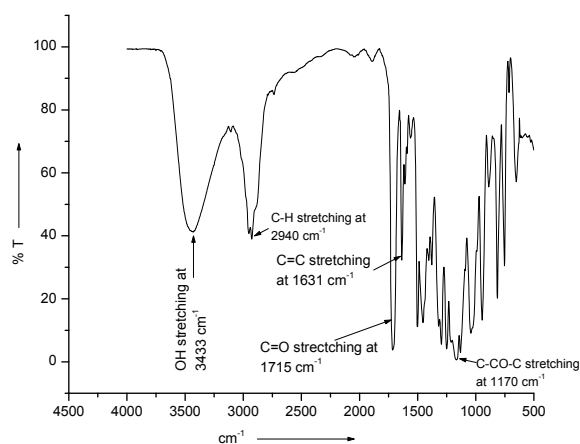


Figure 3: FT-IR of VEOCN

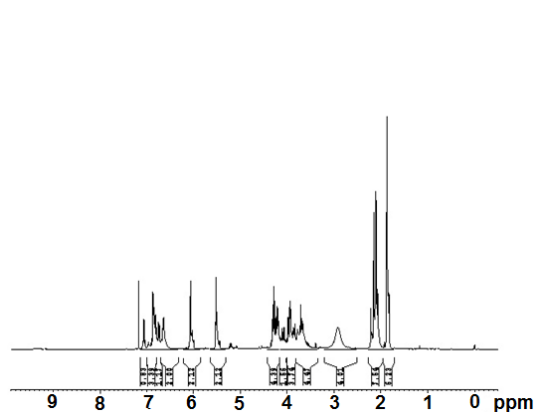


Figure 4:  $^1\text{H-NMR}$  of VEOCN.

## 4. Results And Discussion

Three VER samples (VEOCN, VEMCN, and VEPCN) were prepared using o, m, and p-cresol epoxy novolac resin with acid value  $\sim 7\text{ mg KOH/g}$  solid and used for further studying the curing and decomposition behaviour using styrene (Sty) and methyl methacrylate (MMA) as reactive diluents. Figure 1 shows scheme for the reaction of epoxy novolac with methacrylic acid catalyzed with triphenylphosphene and figure 2 depicts the curing of vinyl ester resin in presence of MMA as reactive diluents and benzoyl peroxide (BP) as free radical initiator.

#### 4.1 Characterization of vinyl ester resin from o-cresol epoxy novolac resin

IR spectrum of vinyl ester resin in figure 3 showed the characteristic broad absorption band due to the secondary hydroxyl group at  $3423\text{ cm}^{-1}$  and peaks at  $1715$  and  $1170\text{ cm}^{-1}$  due to carbonyl groups in the methacrylate ester of vinyl ester resins. The absorption peaks at  $1634\text{ cm}^{-1}$  and  $946\text{ cm}^{-1}$  were due to the stretching and wagging vibrations, respectively, of the C=C in the methacrylate.

$^1\text{H-NMR}$  spectrum of VEOCN in figure 4 showed the vinylic protons resonance signals of the methacrylate group at 5.62 and 6.21 ppm. The resonance signals due to the methyl protons were observed at 2.24 ppm (methyl attached to the aromatic ring) and at 1.99 ppm (methyl of methacrylate group). The signals due to the methylene protons of the polymer backbone as well as the side chain were observed in the region of 3.39-4.15 ppm. Characteristic proton resonance signal due to the secondary hydroxyl group at 4.7 ppm was observed.

#### 4.2 Curing behaviour

The curing behaviour of vinyl ester resins vary with the structure of resins and reactive diluents. Typical DSC scans for the curing of o-cresol novolac based vinyl ester resins (VEOCN) with styrene and methyl methacrylate (40 % w/w), respectively, at a program rate of  $10\text{ }^\circ\text{Cmin}^{-1}$  have been given in Figure 5. It can be observed from the figure that the exothermic transitions for the curing of VEOCN with both the monomers are in the range of  $85 - 150\text{ }^\circ\text{C}$ . The onset temperatures ( $T_i$ ) were  $105.2\text{ }^\circ\text{C}$  and  $93.3\text{ }^\circ\text{C}$  and peak temperature ( $T_p$ ) were  $118.1\text{ }^\circ\text{C}$  and  $100.3\text{ }^\circ\text{C}$  for VEOCN samples containing styrene and methyl methacrylate, respectively. It can be observed that the onset and peak temperature for VEOCN samples containing methyl methacrylate is lower than that of sample containing styrene. This indicates that methyl methacrylate (MMA) is more reactive to VEOCN than styrene during curing in the presence of benzoyl peroxide (BP) as free radical initiator. The reason for this may be attributed to steric factor and greater resonance stability of styrene free radical. Moreover, methyl methacrylate radical is more polar as compared to styrene and thus more reactive.

The onset ( $T_i$ ) and peak temperatures ( $T_p$ ) for o, m and p-cresol novolac based vinyl ester resins (VEOCN, VEMCN and VEPCN) with styrene (STY) monomer have been given in table 1. The data reveals that the peak temperature ( $T_p$ ) of the VEOCN sample containing styrene is the lowest and thus shows rapid curing with styrene monomer as compared to the other two samples. This may be probably due to lower viscosity of VEOCN and greater number of epoxy groups in VEOCN as compared to VEMCN and VEPCN (epoxide equivalent weight; EOCN : 200.3, EMCN : 263.15, EPCN : 233.1), which influence the progress of reaction.

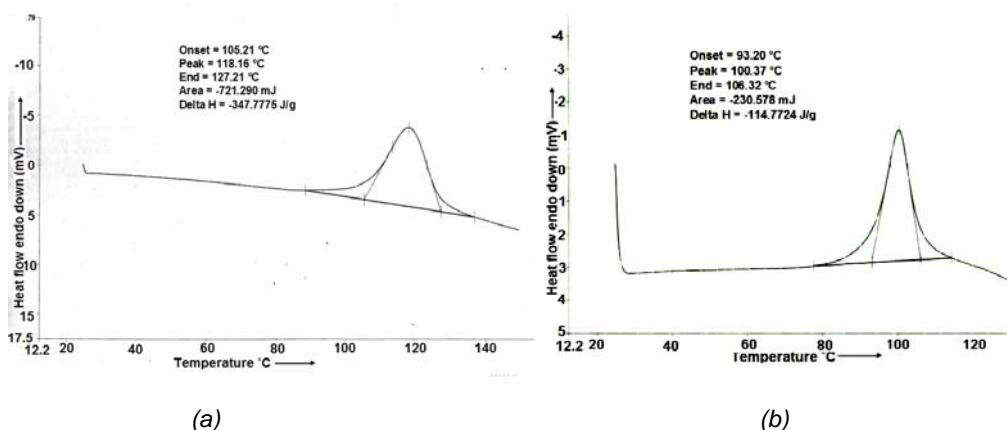


Figure 5: Dynamic DSC for curing at  $10\text{ }^\circ\text{Cmin}^{-1}$  of vinyl ester resin samples (a) VEOCN+Sty (b) VEOCN+MMA

#### 4.3 Thermogravimetric studies

The Typical thermogravimetric (TGA), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) scans for isothermally cured samples of VEOCN with styrene and methyl methacrylate have been shown in figure 6.

Table-1:  $T_i$ ,  $T_p$  and  $T_f$  for curing of samples of VEOCN, VEMCN and VEPCN with styrene.

Sample name	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)
VEOCN+STY	105.06	118.01	127.06
VEMCN+STY	105.22	129.13	139.85
VEPCN+STY	104.10	131.72	143.85

The rate of decomposition at a specific temperature can be determined as the tangential slope of a TGA trace. In general, the temperature at maximum rate of decomposition,  $T_{max}$  is of primary importance. The  $T_{max}$  were 143 °C and 142 °C for cured VEOCN samples containing styrene and methyl methacrylate, respectively. Also on comparing the % weight loss in cured VEOCN sample containing styrene and methyl methacrylate from the figure 7, it is apparent that the thermal stability of sample cured with styrene was higher than sample cured with methyl methacrylate (MMA) due to the presence of aromatic ring of styrene.

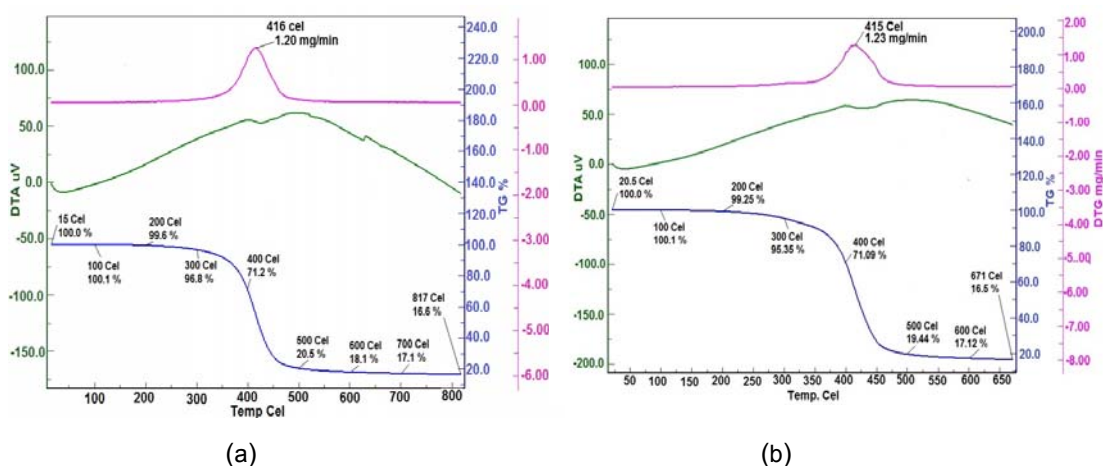


Figure 6: TGA, DTG and DTA scans for cured vinyl ester resin samples (a) VEOCN+STY (b) VEOCN+MMA

VEOCN was selected for studying the decomposition behaviour with different reactive diluents since these resin samples had workable viscosity as compared to VEMCN and VEPCN. The thermogravimetric scans (TGA), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) scans were also performed for VEOCN, VEMCN and VEPCN with styrene and % weight loss of the samples with styrene as monomer have been shown in table 2. It is apparent from the table that the thermal stability of VEOCN cured with styrene as monomer is higher which is in good agreement with the DSC results.

Table 2: Temperature of 1-20 % weight loss of cured samples of VEOCN, VEMCN and VEPCN with styrene in thermogravimetric analysis (program rate 10 °Cmin<sup>-1</sup>)

%wt loss	VEOCN+STY Temp. (°C)	VEMCN+STY Temp. (°C)	VEPCN+STY Temp. (°C)
1	233.85	164.35	178.45
3	296.85	258.65	241.45
4	312.85	279.25	260.45
5	324.85	293.65	275.05
10	360.85	331.55	312.75
20	387.85	364.25	343.35

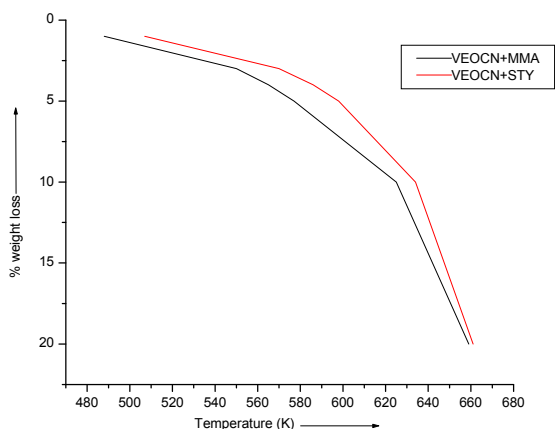


Figure 7: Temperature v/s 1-20 % weight loss of cured samples of VEOCN with styrene and methyl-methacrylate

## 5. Conclusion

In this work, various vinyl ester resin samples VEOCN, VEMCN and VEPCN were prepared by esterification of their corresponding epoxy novolac resins with methacrylic acid in presence triphenylphosphine as catalyst and hydroquinone as inhibitor. Curing and decomposition behaviour of these resins with styrene as reactive diluent were studied using DSC and TGA. On comparing the curing behaviour of VEOCN, VEMCN and VEPCN samples containing styrene as reactive diluent, VEOCN resin sample was found to be the most reactive towards styrene. The result obtained in thermogravimetric studies, also showed isothermally cured sample of the same resin containing styrene to be the most thermally stable. The curing behaviour of VEOCN sample containing methyl methacrylate and styrene as reactive diluents, showed methyl methacrylate to be more reactive as compared to styrene and VEOCN sample containing styrene was again observed to show better thermal stability as compared to that containing methyl methacrylate as reactive monomer, which may be due to the presence of aromatic ring.

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