Olefinic Ester Resins from Maleamic Acids

Elavarasan P, Gopala Krishnan PS* and Nayak SK

Department of Plastics Technology, Central Institute of Plastics Engineering and Technology, TVK Industrial Estate, India

*Corresponding author: PSanthana Gopala Krishnan, Department of Plastics Technology, Central Institute of Plastics Engineering and Technology, TVK Industrial Estate, Guindy, Chennai, India

Abstract

Three different olefinic ester resins were prepared by reacting epoxy resin with monofunctional maleamic acid i.e., N-phenyl maleamic acid and bifunctional maleamic acids namely N-(4-hydroxy phenyl) maleamic acid and N-(4-carboxy phenyl)maleamic acid. These maleamic acid compounds were prepared and characterized by FT-IR, ^{1}H-NMR, proton decoupled ^{13}C-NMR spectroscopic techniques. Reaction of these compounds with epoxy resin followed first order. The activation energy was determined for the reaction of these compounds with epoxy resin and is in the range of 70.9-132.3kJmol^{-1}. Rheological studies on olefinic ester resins indicated Newtonian behavior. Olefinic ester resin derived from monofunctional maleamic acid had lowest viscosity and better shelf life than bifunctional derived. These resins were diluted with 20% styrene and cured using methyl ethyl ketone peroxide and cobalt naphthenate. Thermal stability was evaluated in nitrogen atmosphere and kinetic parameters were determined.

Keywords: Epoxy resin; Characterization; Kinetics; Rheology; Curing; Thermosets

Abbreviations: EA: Activation Energy; CPMA: N-(4-Carboxy Phenyl) Maleamic Acid; CPMOR: CPMA Derived Olefin Ester Resin; DMF: N,N-Dimethyl Formamide; EI: Electron Impact; ΔH*: Enthalpy of Activation; DS*: Entropy of Activation; FT-IR: Fourier Transform Infrared; ΔG*: Free Energy of Activation; A: Frequency Factor; HPMA: N-(4-Hydroxy Phenyl) Maleamic Acid; HPMOR: HPMA Derived Olefin Ester Resin; MEKP: Methyl Ethyl Ketone Peroxide; NMR: Nuclear Magnetic Resonance; PPM: Parts per Million; PMA: N-Phenyl Maleamic Acid; PMOR: PMA Derived Olefinic Ester Resin; TEA: Triethyl Amine

Introduction

Epoxy resins form a family of thermoset resins and are widely used to prepare another thermoset resin namely vinyl ester resin which are generally derived by the addition of ethylenically unsaturated monocarboxylic acid to an epoxy backbone [1-3]. Vinyl ester resins combine the best properties of epoxy and unsaturated polyester resins and are widely used in composites to fabricate a variety of reinforced structures including pipes, tanks, scrubbers and ducts due to their exceptional chemical and corrosion resistance and good mechanical strength. These resins are widely used in coatings, varnishes, adhesives, radiation curable inks, laser video discs, spherical lens materials, molding compounds, structural laminates and specialty coatings for optical fibers, printed circuit boards etc. Currently vinyl ester resins find emerging applications as structural adhesive [4], in wind blade manufacture due to its light weight and corrosion resistance and also in high performance composites for military, marine and biomedical applications.

Various epoxy resins derived from diglycidyl ether of bisphenol A, diglycidyl ether of hydrogenated bisphenol A, diglycidyl ether of tetrabromobisphenol A, diglycidyl ether of bisphenol C [1,1-bis(4-hydroxy phenyl)cyclohexane], Schiffs base as a replacement of bisphenol A, diglycidyl ester of hexahydrophthalic anhydride, novolac based epoxy resin, cardanol based epoxidized novolac resin and rosin resin based epoxy resin, are used to prepare the vinyl ester resins [5-12]. The most commonly used monocarboxylic acid is acrylic acid or methacrylic acid. Acrylic acid is used for coating applications. The methyl group of methacrylic acid stabilizes the ester group toward hydrolysis, and for this reason the methacrylate vinyl esters was found to be more resistant to chemical attack than the acrylate vinyl ester resins, making it suitable for composite applications. Other monocarboxylic acids used are crotonic acid or cinnamic acid [13,14]. Even though, it is improper to use the nomenclature "vinyl ester" for resins derived from crotonic acid or cinnamic acid, it is widely used. Unlike vinyl ester resins derived from methacrylic and acrylic acids, crotonic acid or cinnamic acid incorporate double bonds along the polymer main chain and more appropriate nomenclature would be olefinic ester instead of vinyl ester. The reaction of epoxy resin

with monocarboxylic acid is carried out in the presence of basic catalysts such as triethylamine, tripropylamine, tributylamine, N,N-dimethyl toluidine, N,N-dimethylbenzylamine, pyridine, imidazole, $Sb(Ph)_3$, chromium diisopropyl salicylate and triphenylphosphine [15-22]. Without diluents, viscosities of vinyl ester resins are typically in the range of 1,00,000-8,00,000cps which is too high for many applications. To bring down the viscosity, less viscous reactive diluents such as styrene, α-methyl styrene, vinyl toluene, divinyl toluene, methyl methacrylate, ethyl methacrylate, glycidyl methacrylate, acrylonitrile, dicyclopentadiene diacrylate many of which are too volatile or toxic, are added. Volatile reactive diluents such as styrene has been designated as hazardous pollutant due to high VOC. To reduce emissions, non-volatile reactive diluents such as fatty acid monomers namely methacrylated lauric acid, methacrylated hexanoic acid and lignin based compounds such as methacrylated eugenol, methacrylated guaicol, methacrylated bio-oil [23-25] are suggested for vinyl ester and / or unsaturated polyester resins. These reactive diluents provide crosslink sites and are added in the range of 30 to 50 wt. % [26] to bring down the viscosity in the range of 200 to 2000 cps. It was found that shrinkage of vinyl ester resins during cure increased as styrene concentration in the resin increased. Vinyl ester resins have higher shrinkage of 6 to 9% than epoxy resins [27]. Shrinkage during cure leads to problems such as surface distortion, internal cracks and voids. Therefore there is always a search for newer resins having low viscosities, which in turn will minimize the quantity of reactive diluent. In the present work, epoxy resin was reacted with monofunctional and bifunctional maleamic acids in presence of amine catalyst to prepare olefinic ester resin having amide linkages. To the best of our knowledge, synthesis of thermoset resins from epoxy resin and maleamic acids is not yet reported. Our studies indicated that olefinic ester resin derived from monofunctional has lowest viscosity, thereby minimizing the amount of reactive diluents required to alter the viscosity to the working range.

Experimental

Materials

Maleic anhydride, aniline, 4-aminophenol and 4-amino benzoic acid, triethyl amine (TEA) and N,N-dimethyl formamide (DMF) were purchased from Sigma-Aldrich. Epoxy resin Joncryl ADR 4380 (epoxy equivalent weight 455) was purchased from BASF. Toluene, acetone and styrene were received from Merck. All solvents were dried according to the standard procedures prior to use.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000 to 400cm^{-1} at room temperature using a Thermo Scientific model Nicolet 6700. A Jeol 500MHz Nuclear Magnetic Resonance (NMR) spectrometer was used for recording ^{1}H-NMR and proton decoupled ^{13}C-NMR spectra at room temperature using DMSO-d$_6$ as solvent and tetramethylsilane as an internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Electron impact (EI) mass spectra were recorded using a Micromass VG 7035. Ionisation potential of 70eV was used for EI mode. Rheological studies were carried out using Haake Mars/ Modular Advanced Rheometer System (Thermo Scientific). A Brookfield Digital Viscometer (Model DV-2) was used to measure the viscosities of olefinic ester resins at 25 °C. Thermal stability of cured resin was evaluated using Perkin Elmer TGA Pyris 7 at a heating rate of 10 °C min^{-1} in nitrogen atmosphere and sample size of 10±1mg was used.

Synthesis of maleamic acids

Aniline (500mmol, 46.5g) was charged in a 500mL two-necked round bottomed flask and dissolved in 200mL of pre-dried acetone. The flask was placed over a crushed ice bath and magnetic stirrer was used to stir the reaction mixture. Maleic anhydride (500mmol, 49.0g) was added in portions over 30min. After addition of maleic anhydride was over, the solution gradually changed into yellow orange slurry. The reaction was continued for two hours. Yellow coloured powder was obtained. The slurry was filtered under suction and washed with acetone to obtain pure N-phenyl maleamic acid (PMA) [28] and dried at 60 °C for 90min. Yield obtained was 98%. The melting point observed by DSC was 212 °C. Similar procedure was followed for the preparation of N-(4-hydroxy phenyl) maleamic acid (HPMA) [29] and N-(4-carboxy phenyl) maleamic acid (CPMA) [30] using 4-aminophenol and 4-amino benzoic acid instead of phenol respectively. In the case of CPMA, DMF was used as solvent instead of acetone. Both HPMA and CPMA were in yellow color (yield 97%). Melting point of HPMA and CPMA observed by DSC was 215 and 223 °C respectively. NMR spectra of PMA, HPMA and CPMA are given in (Figures 1-3).
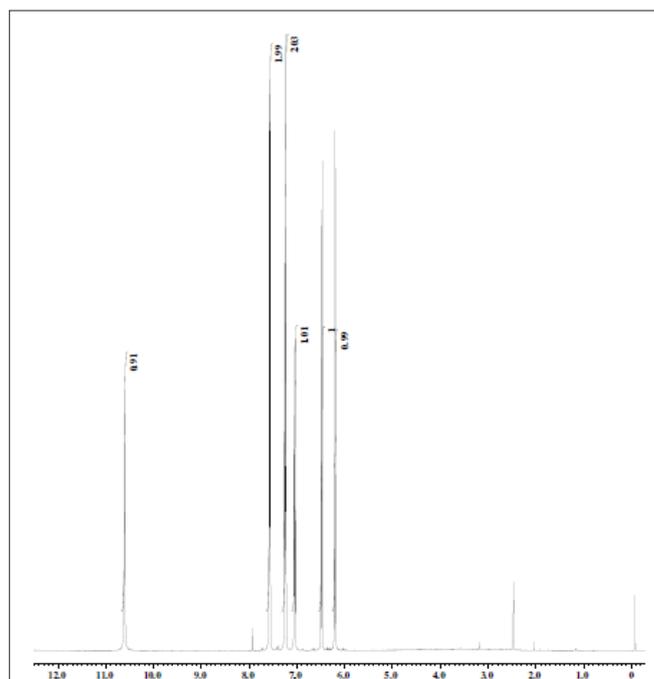

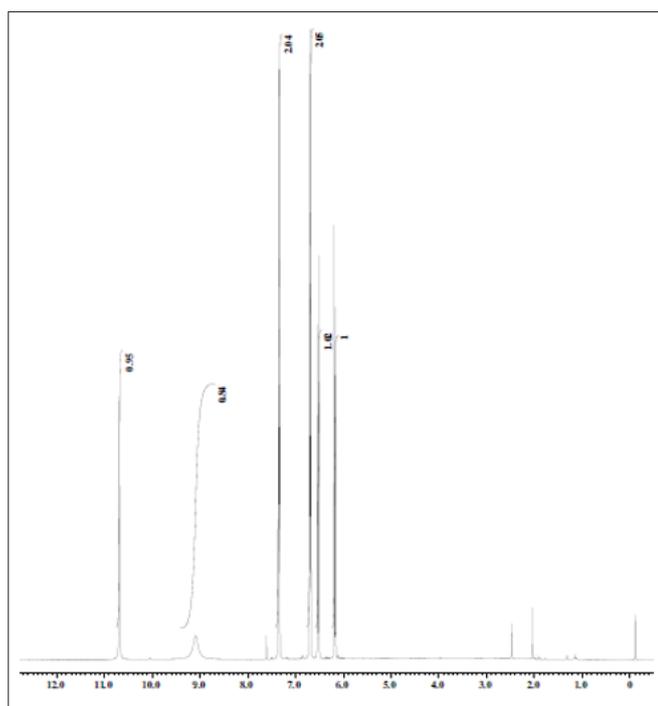**Figure 1:** ^{1}H-NMR spectrum of PMA.

c. **^{13}C-NMR** (DMSO-d_6,δ): 120.5 (Ar C ortho to NH), 124.1(Ar C para to NH), 129.1(Ar C meta to NH), 130.3 (=$\underline{C}$HCOOH), 132.7($\equiv\underline{C}$NH), 138.2 (=$\underline{C}$HCONH), 164.1 ($\underline{C}$ONH), 166.3 ($\underline{C}$OOH) EI-MS (m/z): 192 (M+1)

HPMA

a. **FT-IR** (cm^{-1}): 3293 (u$_{O-H}$), 3200 (u$_{N-H}$), 3061,2816 (υ$_{C-H}$), 1695 (υ$_{C=O}$), 1608 (υ$_{C=C}$), 1530 and 1457 (u$_{Phenyl}$).

b. **^{1}H-NMR** (DMSO-d_6,δ): 6.2 (d,1H, CH=C$\underline{H}$COOH), 6.5 (d,1H, CH=C$\underline{H}$CONH),) 6.7 (d,2H, Ar H meta to NH), 7.2 (d, 2H, Ar H ortho to NH), 9.1 (b, 1H,O$\underline{H}$) , 10.6 (s,1H, COO$\underline{H}$).

c. **^{13}C-NMR** (DMSO-d_6,δ): 115.7 (Ar C meta to NH), 122.6 (Ar C ortho to NH), 155.5 (Ar C para to NH), 128.8 ($\equiv\underline{C}$NH), 133.2(=$\underline{C}$HCOOH), 134.5 (=$\underline{C}$HCONH), 163.9 ($\underline{C}$ONH), 165.7 ($\underline{C}$OOH) EI-MS (m/z): 208 (M+1)

CPMA

a. **FT-IR** (cm^{-1}): 3293 (u$_{O-H}$), 3061 (u$_{N-H}$), 2816 (υ$_{C-H}$), 1690 (υ$_{C=O}$), 1601 (υ$_{C=C}$), 1530 and 1450 (u$_{Phenyl}$).

b. **^{1}H-NMR** (DMSO-d_6,δ): 6.2 (d,1H, CH=C$\underline{H}$COOH) 6.4 (d,1H, CH=C$\underline{H}$CONH) 7.7 (d, 2H, Ar H ortho to NH) 7.8 (d,2H, Ar H meta to NH), 8.1 (b, 1H,N$\underline{H}$), 10.6 (b,1H, Ar COO$\underline{H}$), 12.1 (b,1H, =CHCOO$\underline{H}$).

c. **^{13}C-NMR** (DMSO-d_6,δ): 119.3(Ar C ortho to NH), 126.4(Ar C para to NH), 130.7 (Ar C meta to NH), 131.1(=$\underline{C}$HCOOH),132.3(=$\underline{C}$HCONH), 142.6($\equiv\underline{C}$NH), 164.2($\underline{C}$ONH), 167.1(Ar $\underline{C}$OOH), 167.5(=CH$\underline{C}$OOH) EI-MS (m/z): 235 (M$^+$)

Synthesis of olefinic ester

To a 250mL three necked round bottom flask fitted with a reflux condenser and nitrogen inlet, 200mmol of PMA was added to 90mL of DMF:THF (1:2V/V) solvent mixture. PMA was dissolved by stirring and heating at 50 °C for 10min to get homogeneous solution. Epoxy resin, Joncryl ADR 4380 (0.2 times of its epoxy equivalent weight) was gradually added. Reaction mixture was stirred well using magnetic stirrer, then 20mmol of TEA catalyst was added to the solution [31]. Nitrogen gas was purged and refluxed for 8h to get PMA derived olefinic ester resin (PMOR). Reaction mixture was cooled to room temperature and washed with distilled water to remove the catalyst. Washing was repeated until the pH was neutral. Then the resin was dissolved in dichloromethane to remove the trapped water. Using separating funnel, water which floated as upper layer was removed. Solvent was removed by applying vacuum followed by drying at 60 °C for few hours. Resin was stored in refrigerator till its use. The above procedure was followed for preparing HPMA and CPMA derived olefinc ester resins namely HPMOR and CPMOR respectively (Figure 4). Hydroxyl group of HPMA and carboxyl group of CPMA would react with epoxy group in addition to the maleamic acid group. As both HPMA and CPMA are being bifunctional, twice the quantity of epoxy resin was used to synthesize HPMOR and CPMOR.

Figure 2: ^{1}H-NMR spectrum of HPMA.

Figure 3: ^{1}H-NMR spectrum of CPMA.

PMA

a. **FT-IR** (cm^{-1}): 2900-3200 (u$_{O-H}$), 3271 (u$_{N-H}$), 3036(υ$_{C-H}$), 1694 (υ$_{C=O}$), 1618 (υ$_{C=C}$), 1535 (u$_{Phenyl}$).

b. **^{1}H-NMR** (DMSO-d_6,δ): 6.2 (d,1H, C$\underline{H}$=CHCOOH), 6.5 (d,1H, CH=C$\underline{H}$CONH), 7.2 (t,1H, Ar H para to NH), 7.3 (t,2H, Ar H meta to NH), 7.6 (d,2H, Ar H ortho to NH), 8.0 (b, 1H,N$\underline{H}$), 10.6 (s,1H, COO$\underline{H}$).
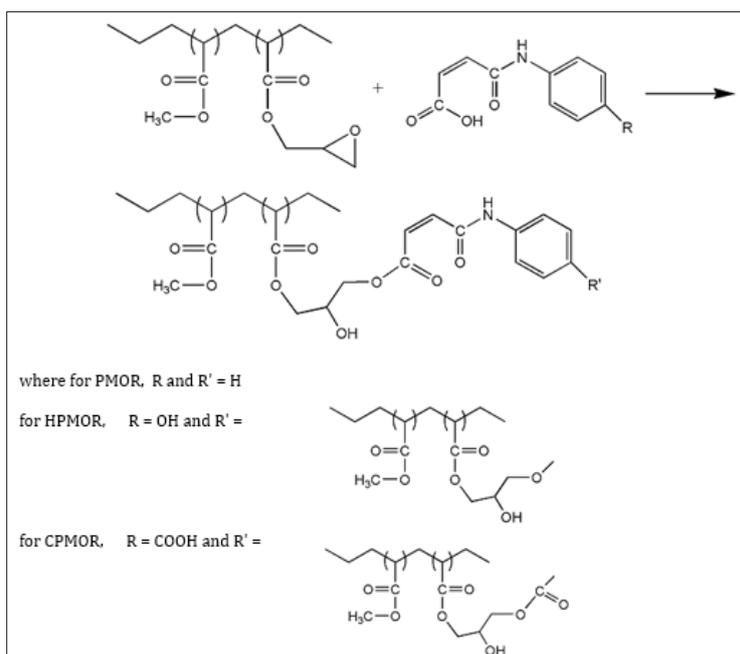
Figure 4: Preparation of olefinic esters.

PMOR

a. **¹H-NMR** (DMSO-d$_6$, δ in ppm): 1.1, 1.29, 1.4, 2.4, 3.5, 4.0, 6.9, 7.1, 7.2, 7.3, 7.46, 7.9.

b. **¹³C-NMR** (DMSO-d$_6$, δ in ppm): 13.9, 19.2, 30.6, 67.5, 127.3, 128.2, 129.2, 129.3, 135.1, 162.8, 170.4.

HPMOR

a. **¹H-NMR** (DMSO-d$_6$, δ in ppm): 1.1, 1.3, 1.4, 1.7, 2.15, 3.5, 4.0, 6.8, 7.0 and 7.9.

b. **¹³C-NMR** (DMSO-d$_6$, δ in ppm): 13.9, 19.2, 30.6, 67.5, 115.9, 122.9, 128.9, 135.0, 162.8, 170.0, 174.3.

CPMOR

a. **¹H-NMR** (DMSO-d$_6$, δ in ppm): 1.1, 1.29, 1.4, 1.7, 2.15, 3.5, 4.0, 6.8, 7.0, 7.9.

b. **¹³C-NMR** (DMSO-d$_6$, δ in ppm):13.9, 19.2, 30.6, 67.5, 116, 123, 124, 135.1, 162.8, 170.0, 174.3.

Kinetics

The reaction of PMA, HPMA, CPMA with epoxy resin at various temperatures 50 °C, 60 °C, 70 °C was studied in order to determine the kinetic parameters such as rate constant and activation energy. The reaction was monitored by determining acid number potentiometrically. To a 250mL three necked round bottom flask, 10g (52.4mmol) of PMA pre-dissolved in 20mL DMF was charged and the flask was fitted with a condenser and a nitrogen inlet. 23.82g (52.4mmol) of epoxy resin pre-dissolved in 30mL of DMF was gradually added. To this reaction mixture, 1g of TEA catalyst was added and the time was taken as to. Solution was stirred using a magnetic stirrer and reaction was carried out at a specific temperature. Aliquots of reaction mixture were taken at various intervals of time. To determine acid number the reaction mixture was potentiometrically titrated against standardized ethanolic KOH. Acid number is expressed as mg of KOHg^{-1} and determined using the following equation.

Acid Number=(56.1 x V x N)/W

where 'N' is the normality of KOH solution, 'V' is the KOH used for reaction mixture (mL), and 'W' is the weight of maleamic acid present in the reaction mixture (g).

Shelf life

Viscosity of PMOR, HPMOR, CPMOR resins was measured using Brookfield viscometer at 25 °C and 50±5% RH as per ASTM 1824 method. Viscosity was measured at various intervals of time to determine the shelf life of these resins. 90mL of the resin was taken in a 100mL beaker for the viscosity measurement and the resin was allowed to equilibrate at the test temperature to avoid the variation in viscosity due to temperature fluctuation.

Rheology

Rheological behavior of PMOR, HPMOR and CPMOR was analyzed by rotational viscometer to study the effect of viscosity as a function of shear rate. The resins used for the study were free from solvent and moisture and measurements were made at room temperature. Few drops of the resin was taken at the round bottom plate of rotational viscometer and is subjected to shear by means of upper and bottom plates and gap was fixed at 0.1mm. Test time for each sample was 60s at fixed shear rate 2, 4, 6, 8 and10rads^{-1} at 25 °C.

Curing

PMOR, HPMOR and CPMOR resins were diluted with 20% of styrene by weight, which acts as cross-linking agent in forming three dimensional network. Methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate were used as curing agent and accelerator, respectively. After thorough mixing of curing agent and accelerator, resins were cured at 80 °C for 10h followed by post curing at 110 °C for 8h.

Results and Discussion

Characterization

FT-IR spectrum of olefinic ester resins showed the disappearance of peak corresponding to epoxy group at 908cm⁻¹ indicating that the epoxy group had reacted [32]. In PMOR and CPMOR resin, addition reaction between epoxy resin and amic acid/carboxylic acid groups, led to the formation of ester groups. In the case of HPMOR, in addition to the formation of ester linkage, epoxy resin had also reacted with hydroxyl group of HPMA to form an ether linkage. ¹H-NMR spectrum of CPMA, epoxy resin and CPMOR is given in (Figure 5). In the CPMOR spectrum, the absence of -COOH peak in the region of 10 to 12ppm indicated that the carboxylic acid group had reacted with the epoxy group completely. Aromatic proton peaks of maleamic acid compound in the range of 7 to 8ppm were present. Similar behavior was observed in the NMR spectra of PMOR and HPMOR resins. Absence of peaks above 8ppm indicated that the amic acid group of PMA and HPMA and the hydroxyl group of HPMA had reacted with the epoxy resin. The cured resins were characterized by IR spectroscopy technique. All the cured olefinic ester resins showed a disappearance of peak at 1600cm⁻¹ which is the characteristic peak of alkene double bond. This confirmed the opening of the double bond during the curing of the resin.
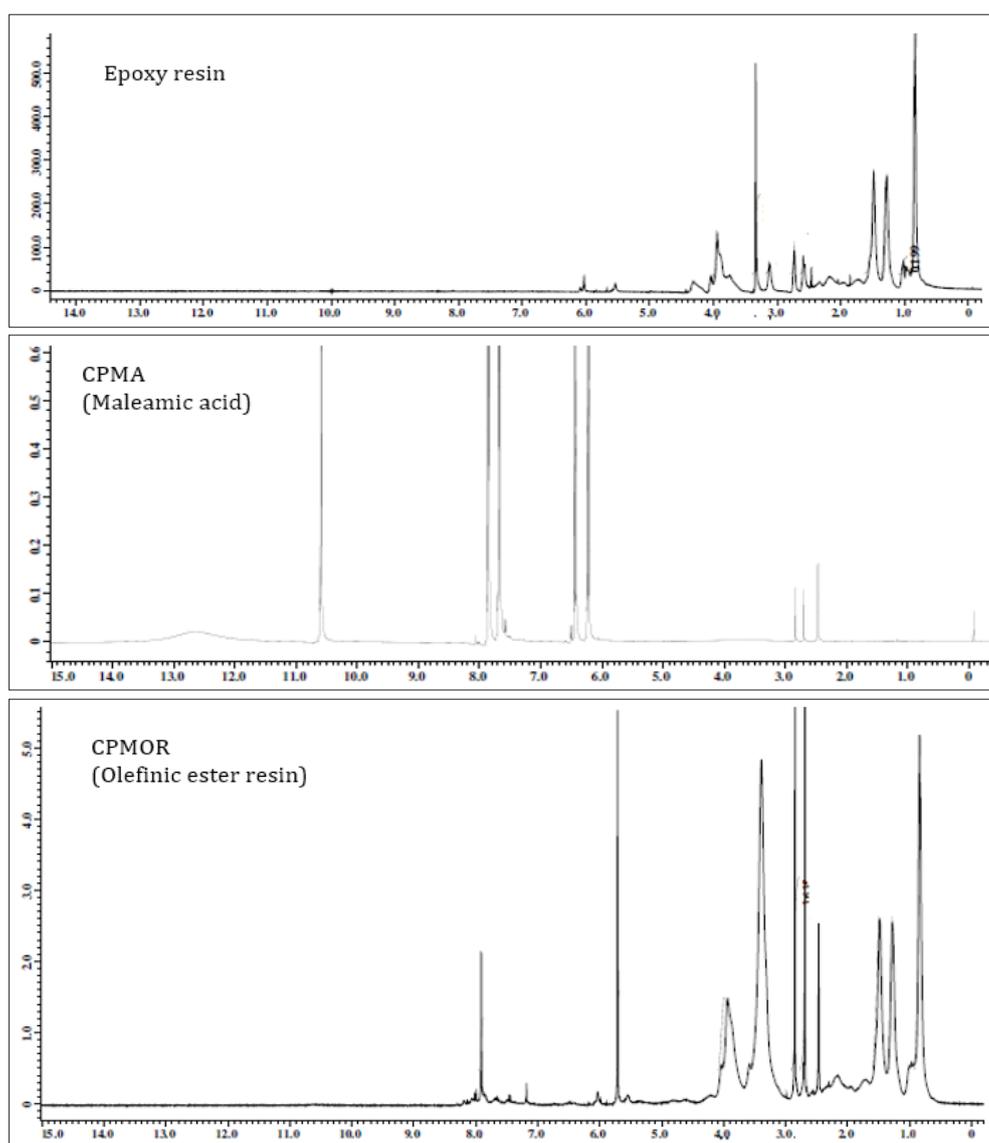

Figure 5: ¹H-NMR spectra of epoxy resin, CPMA maleamic acid and CPMOR olefinic ester resin.

Kinetics

Several researchers have reported the kinetics of reaction of methacrylic acid with epoxy resin using different catalysts such as tertiary amines, triphenylphosphine. They reported that rate of the reaction was found to be first order with respect to acid concentration and the reaction followed first order kinetics [11,16,33-36]. The first order rate equation is given as follows:

$$k = \frac{1}{t} \ln \left(\frac{a}{a-x} \right)$$

where, 'k' is the first order rate constant, 'a' is the initial concentration of the maleamic acid and 'x' is the concentration of the maleamic acid at time 't'. Rate constant at three different temperatures were calculated from the slope of the plot ln (a/(a-x)) vs. t. The rate constants at various temperatures for the maleamic acids are given in (Table 1). For the given maleamic acid derived olefinic ester resin, rate constant increased with increase in temperature. At a given temperature, rate constant of CPMA was higher than PMA which indicated the aromatic carboxylic acid group was more reactive than amic acid group. Among the bifunctional maleamic acids, the rate constant for the reaction of epoxy resin with HPMA was lower when compared to that of CPMA at a given temperature, indicating the competing etherification reaction influenced the rate of esterification. Activation energy (E_a) and frequency factor (A) were calculated using an Arrhenius equation.

$$k = A \exp^{\left(\frac{-E_a}{RT} \right)}$$

Table 1: Rate constants for the reaction of epoxy resin with maleamic acids at different temperatures.

Maleamic Acid	Rate Constant (min⁻¹) at Different Temperatures (°K)		
	323	333	343
PMA	0.029	0.095	0.134
HPMA	0.019	0.031	0.343
CPMA	0.033	0.269	0.419

Rate constants were found to obey Arrhenius equation. E_a was then determined using the above equation by plotting ln k vs 1000/T where T is the temperature at which the reaction was carried out. E_a of PMOR was comparable with that of vinyl ester resin derived from acrylic acid and monoepoxy compound in the presence of triphenyl phosphine as catalyst [35,36]. Even though both HPMA and CPMA are bifunctional, HPMA was found to have higher E_a than CPMA which indicated that esterification reaction in HPMA required more energy for the reaction to take place due to the competing etherification reaction. E_a of HPMOR was comparable with that of vinyl ester resin derived from methacrylic acid and cardanol based epoxidized novolac resin in the presence of triphenyl phosphine as catalyst [11].

Entropy of activation (DS⁺), Enthalpy of activation (ΔH⁺) and free energy of activation (ΔG⁺) were calculated using the following equations

$$k = \frac{k_b T}{h} e^{\left(\frac{-E_a}{RT} \right)} e^{\left(\frac{\Delta S^{\neq}}{R} \right)}$$

where k_b is Boltzmann constant and h is Plank's constant.

ΔH⁺=E_a-RT

ΔG⁺=ΔH⁺-TDS⁺

Thermodynamic parameters (DS⁺, ΔH⁺ and ΔG⁺) for the reaction of epoxy resin with PMA, HPMA and CPMA are reported in (Table 2). DS⁺ and ΔG⁺ for PMA were found to be negative and positive respectively. As DS⁺<0 and ΔG⁺>0 for the reaction of epoxy resin with PMA, indicated that the formation of highly ordered activated complex in the synthesis of olefinic ester resin and process is spontaneous and irreversible respectively. Similar observations with respect to DS⁺ and ΔG⁺ were reported for the reaction of epoxy resin with acrylic acid/methacrylic acid in the presence of tertiary amine/triphenyl phosphine catalyst [6,22,35,36]. ΔH⁺ value of CPMA is lower than that of HPMA which again indicated that aromatic hydroxyl group in HPMA is less reactive than carboxyl group in aromatic ring. Positive DS⁺ indicated that transition state is achieved through dissociative mechanism in the reaction between bifunctional maleamic acid and epoxy resin.

Table 2: Kinetic parameters for the reaction of epoxy resin with maleamic acids.

Maleamic Acid	E_a (KJ/mole)	ln A (min⁻¹)	ΔH⁺ (KJ/mole)	ΔS⁺ (J/Kmole)	ΔG⁺ (KJ/mole)
PMA	70.9	22.97	68.1	-88.7	156.9
HPMA	132.3	44.99	129.5	94.1	35.4
CPMA	117.7	40.69	114.9	58.3	56.6

Shelf life

Viscosity data of olefinic ester resins is tabulated in (Table 2) as a function of time at room temperature. Viscosity of PMOR was lower than the viscosity value of HPMOR and CPMOR. Bifunctional maleamic acid compounds HPMA and CPMA enhanced the viscosity of HPMOR and CPMOR resins enormously, which indicated that substantial entanglement had taken place. Viscosity of HPMOR was higher than that of CPMOR. It was reported that the extent of increase in the viscosity is higher in etherification reaction when compared to esterification reaction [10]. Therefore, in HPMOR the etherification reaction between hydroxyl group and epoxy group increased the viscosity drastically than CPMOR where only esterification reaction could take place.

Rheological study

The shear stress at various shear rates was determined for olefinc ester resins and is given in (Figure 6). This shows a linear

response of the shear stress to the shear rate which confirmed that PMOR, HPMOR, CPMOR and the base epoxy resin from which these olefinic ester resins were derived exhibited a Newtonian Behaviour. The slope of shear stress vs. shear rate decreases in the following order: HPMOR>CPMOR>PMOR, which indicated that the viscosity of HPMOR is higher than CPMOR followed by PMOR.
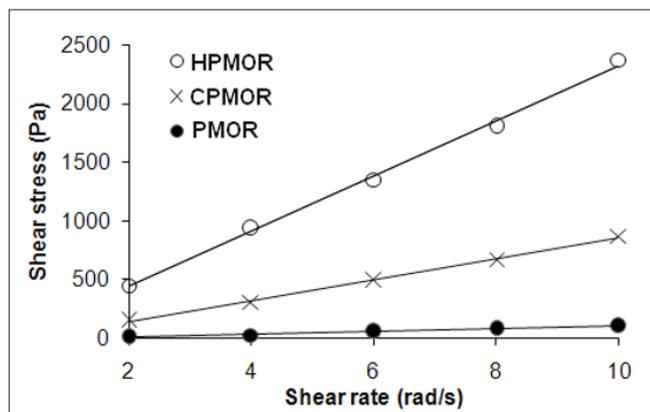

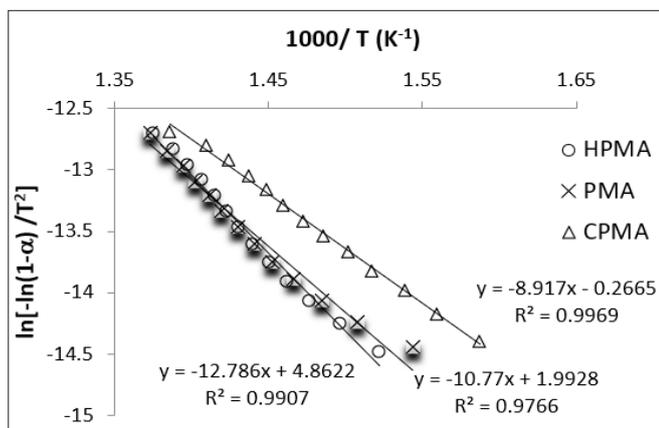**Figure 6:** Plot of shear stress vs. shear rate for olefinic ester resins.

Thermal stability

Figure 7: Plot of ln[-ln(1-α)/T2] vs. 1000/ T of olefinic ester resins.

Cured resins of PMOR, HPMOR and CPMOR showed single step degradation in nitrogen atmosphere. Cured resins were stable up to 250 °C and started losing weight above this temperature. Rapid thermal degradation was observed in the temperature range of 350 to 500 °C and almost total volatilization of the sample occurred at about 700 °C. Temperature at which 10% weight loss and maximum rate of thermal degradation (T_{max}) of cured resins indicated that thermal stability decreased in the following order: HPMOR cured>PMOR cured>CPMOR cured (Figure 7). Coats-Redfern [37] method was used to determine the activation energy for thermal degradation of cured resins and the equation used is given below:

$$\ln\left[\frac{-\ln\left(1-\alpha\right)}{T^2}\right] = \ln\left(\frac{AR}{\phi E_a}\right)\left[1-\left(\frac{2RT}{E_a}\right)\right] - \left(\frac{E_a}{RT}\right)$$

where α is the fraction decomposed at temperature T, Ø is the heating rate, E_a is the activation energy for thermal decomposition reaction, R is the universal gas constant and A is the Arrhenius frequency factor. When the order of reaction is one, then the plot of ln[-ln(1-α)/T²] vs. 1000/T gives a straight line with slope equivalent to -E_a/R. Plot of ln[-ln(1-α)/T²] vs. 1000/T gave a straight line suggesting that decomposition followed first order kinetics in nitrogen atmosphere. Activation energy calculated from the slope of these curves is given in (Table 3). Activation energy for thermal degradation of HPMA cured resin was found to be higher than PMA followed by CPMA cured resins, which indicated that HPMA cured resin was having higher thermal stability than PMA followed by CPMA (Table 4).

Conclusion

Monofunctional maleamic acid PMA and bifunctional maleamic acid CPMA had undergone esterification whereas bifunctional maleamic acid HPMA had undergone both esterification and etherification reaction with epoxy resin to form olefinic ester resin, which was confirmed by IR and NMR characterization. Addition reaction of maleamic acid compounds with epoxy resin followed first order kinetics. Viscosity of monofunctional maleamic acid derived olefinic ester resin was lower than that of bifunctional maleamic acid, which suggested lesser requirement of reactive diluent for monofunctional maleamic acid. All resins showed Newtonian behavior. Cured resins showed single step thermal degradation in nitrogen atmosphere.

Table 3: Viscosity (cPs) as a function of time. a-using spindle #4, b-using spindle #6.

Days	PMOR[a]	HPMOR[b]	CPMOR[b]
Initial	7560	86800	63100
2	8530	88150	68650
4	9440	93450	75450
7	10580	99800	81200
30	14980		

Table 4: Thermal degradation data.

Cured Resin	10% Weight Loss (°C)	T_{max} (°C)	E_a (kJ/mole)
PMOR	322.5	423	89.5
HPMOR	339.7	426	106.2
CPMOR	313.6	421	74.1

References

1. Yebassa D, Balakrishina S, Feresenbet E, Raghvan D, Start PR, et al. (2004) Chemically functionalized clay vinyl ester nanocomposites: Effect of processing parameters. Journal of Polymer Science Part A: Polymer Chemistry 42(6): 1310-1321.

2. Chaudhary J, Dadhich S, Jinger S, Tailor G (2017) Epoxy based vinyl ester resins: Synthesis and characterization. International Journal of Chemical Engineering Research 9(1): 99-104.

3. Malik M, Choudhary V, Varma IK (2000) Current status of unsaturated polyester resins. Journal of Macromolecular Science: Review in Macromolecular Chemistry & Physics C 40(2&3): 139-165.

4. Ambrogi V, Carfagna C, Giamberni M, Amendola E, Douglas EP (2002) Liquid crystalline vinyl ester resins for structural adhesives. Journal of Adhesion Science & Technology 16(1): 15-32.

5. Auad ML, Frontini PM, Borrajo J, Aranguren MI (2001) Liquid rubber modified vinyl ester resins: Fracture and mechanical behavior. Polymer 42(8): 3723-3730.

6. Siva P, Varma IK, Patel DM, Sinha TJM (1994) Effect of structure on properties of vinyl ester resins. Bulletin of Material Science 17(6): 1095-1101.

7. Kagathara VM, Parsania PH (2002) Thermal analysis of cured chloro epoxy resins and epoxy-acrylaye-styrene copolymers. Polymer Testing 21(6): 659-663.

8. Langer E, Waskiewicz S, Kuczynska H (2019) Application of new modified schiff base epoxy resin as organic coatings. Journal of Coatings Technology and Research. 16: 1109-1120.

9. Agarwal N, Singh A, Varma IK, Choudhary V (2008) Effect of structure on mechanical properties of vinyl ester resins and their glass fiber-reinforced composites. Journal of Applied Polymer Science 108(3): 1942-1948.

10. Scott TF, Cook WD, Forsythe JS (2002) Kinetics and network structure of thermally cured vinyl ester resins. European Polymer Journal 38(4): 705-716.

11. Sultania M, Rai JSP, Srivastava D (2010) Kinetic modeling of esterification of cardanol-based epoxy resin in the presence of triphenylphosphine for producing vinyl ester resin: Mechanistic rate equation. Journal of Applied Polymer Science 118(4): 1979-1989.

12. Atta AM, Mansour R, Abdou MI, Sayed AM (2004) Epoxy resins from rosin acids: Synthesis and characterization. Polymers for Advanced Technologies 15(9): 514-522.

13. Bratychak MW, Dukh OI, Brzozowski ZK (1997) Synthesis of oligomers with unsaturated end-groups based on dianic epoxy resin and crotonic acid. Journal of Macromolecular Science Part A: Pure & Applied Chemistry A 34(2): 389-396.

14. Zaske OC (1998) Unsaturated polyester and vinyl ester resin in Goodman SH editor Handbook of Thermoset Plastics, New Jersey: William Andew, USA. pp. 122-168.

15. Agrawal S, Singhal R, Rai JSP (1999) Curing and rheological behavior of vinyl ester resins prepared in the presence of tertiary amines. Journal of Macromolecular Science Part A: Pure & Applied Chemistry 36(5-6): 741-757.

16. Srivastava A, Pal N, Agrawal S, Rai JSP (2005) Kinetics and mechanism of esterification of epoxy resin with methacrylic acid in the presence of tertiary amines. Advances in Polymer Technology 24(1): 1-13.

17. Malik M, Choudhary V, Varma IK (2002) Effect of non-halogen flame retardant additives on the properties of vinyl ester resins and their composites. Journal of Fire Science 20(4): 329-342.

18. Jaswal S, Gaur B (2014) New trends in vinyl ester resins. Reviews in Chemical Engineering 30(6).

19. Rao BS, Madec PJ, Marechal E (1986) Synthesis of vinyl ester resins. Polymer Bulletin 16(2-3): 153-157.

20. Robinette EJ, Ziaee S, Palmese GR (2004) Toughening of vinyl ester resin using butadiene-acrylonitrile rubber modifiers. Polymer 45(18): 6143-6154.

21. Sandner B, Schreiber R (1992) Synthesis and polymerization of epoxymethacrylates, 1. Catalysis and kinetics of the addition reaction of methacrylic acid and 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane. Die Makromolecular Chemie 193(11): 2763-2770.

22. Srivastava A, Agarwal S, Rai JSP (2002) Kinetics of esterification of cycloaliphatic epoxies with methacrylic acid. Journal of Applied Polymer Science 86(13): 3197-3204.

23. La Scala JJ, Sands JM, Orlicki JA, Robinette EJ, Palmese GR (2004) Fatty acid-based monomers as styrene replacements for liquid molding resins. Polymer 45(22): 7729-7737.

24. La Scala JJ, Jeyarajasingam A, Logan MS, Winston C, Myers P, et al. (2007) Fatty acid-based vinyl ester composites with low hazardous air pollutant content. Journal of Biobased Materials and Bioenergy 1(3): 409-416.

25. Stanzione JF, Giangiulio PA, Sadler JM, La Scala JJ, Wool RP (2013) Lignin-based bio-oil mimic as biobased resin for composite applications. ACS Sustainable Chemistry & Engineering 1(4): 419-426.

26. Brill RP, Palmese GR (2000) An investigation of vinyl-ester-styrene bulk copolymerization cure kinetics using Fourier transform infrared spectroscopy. Journal of Applied Polymer Science 76(10): 1572-1582.

27. Dudgeon CD (1985) in Handbook of Composites. In: Watt W, Perov BV (Ed.), Qbsevier Sci. Publications, New York.

28. Cava MP, Deana AA, Muth K, Mitchell M (1961) N-phenyl maleimide. Organic Syntheses 41: 93-95.

29. Wu CS, Liu YL, Hsu LKY (2003) Maleimide-epoxy resins: Preparation, thermal properties, and flame retardance. Polymer 44(3): 565-573.

30. Oishi T, Iwahara M, Fujimoto M (1991) Polymerization and copolymerization of N-(4-carboxyphenyl) maleimide. Polymer Journal 23(12): 1409-1417.

31. White LA, Weber JW, Mathias LJ (2001) Synthesis and thermal characterization of a one component maleimide-epoxy resin. Polymer Bulletin 46(5): 463-469.

32. In: Dyer JR (ed.), (1997) Application of absorption spectroscopy of organic compounds. Prentice-Hall: New Delhi, India. pp. 22-57.

33. Rafizadeh M, Ghasemi H, Haddadi Asl V (2006) Kinetic modeling of esterification of epoxy resin in the presence of triphenylphosphine for producing vinyl ester resin: Mechanistic rate equation. Chinese Journal of Polymer Science 24(6): 599-608.

34. Hamedani GH, Ebrahimi M, Ghaffarian SR (2006) Synthesis and kinetics study of vinyl ester resin in the presence of triethyl amine. Iranian Polymer Journal 15(11): 871-878.

35. Pal N, Srivastava A, Rai JSP (2004) Kinetics and mechanism of esterification of epoxy resin in presence of triphenylphosphine. International Journal of Chemical Kinetics 36(5): 280-285.

36. Pal N, Srivastava A, Agarwal S, Rai JSP (2005) Kinetics and mechanism of esterification of monoepoxies. Materials & Manufacturing Processes 20(2): 317-327.

37. Coats AV, Redfern JP (1964) Kinetic parameters from thermogravimetric data. Nature 201: 68-69.

For possible submissions Click below:

Submit Article