

Bio-based epoxy thermosets with rosin derived imidoamine curing agents and their structure-property relationships

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Received 11 July 2019; accepted in revised form 14 September 2019

Abstract. Multifunctional bio-based epoxy resin (PEMPAE) was synthesized by reacting Diels-Alder adduct of gum rosin and maleic anhydride (MPA) with pentaerythritol to get the esterified product (PEMPA) which was further epoxidized using epichlorohydrin and potassium hydroxide. This paper includes the synthesis of bio-based imidoamine curing agent (IAEDK) by reacting diamino diphenyl ether (DDE) with dimaleopimaryl ketone (DMPK), a dehydrodecarboxylated derivative of MPA. The synthesized products were characterized by Fourier transform infrared Spectroscopy (FTIR), proton and ^{13}C nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$). Curing dynamics of rosin-based epoxy cured with rosin-based imidoamine crosslinker were evaluated using differential scanning calorimetry (DSC) and were compared with resin cured with synthesized DMPK and commercial DDE curing agents. The mechanical properties and thermal stability of the cured epoxy samples were evaluated using a universal testing machine (UTM) and thermogravimetric analyzer (TGA), respectively. The chemical resistance of the samples was determined in terms of % weight loss when immersed in NaOH, HCl and NaCl solutions. The morphological changes were also evaluated via scanning electron microscopy (SEM). Results revealed that rosin-based epoxy cured with imidoamine curing agent gave preeminent properties over the commercial one. The studies suggested that curing properties were greatly affected by the molecular topology and kind of curing agent used.

Keywords: thermosetting resins, rosin, bio-based epoxy, imidoamine curing agent, thermal properties

1. Introduction

Dwindling petroleum resources and growing environmental concerns have led the modern-day polymer technologist to explore the utilization of bio-based scaffolding materials for polymers as an alternative. Rosin, obtained from pine trees, is an abundant bio-based material having the potential of chemical modification. It consists of a mixture of pimaric (30–40%) and abietic type (20–30%) acids along with a smaller fraction of neutral components (10–20%). The inherent acid groups and double bonds in their moiety facilitate it to be transformed into a variety of derivatives such as salts, hydrogenated and decarboxylated rosins, esters, and anhydride adducts [1]. The chemically modified rosin is frequently used in manufacturing paints, varnishes, adhesive tackifiers,

paper sizing agents, solders and fluxes, electronic insulating materials, printing inks, soaps, etc. [2]. Much focus these days is to exploit bio-based raw material for the synthesis of new materials with specific chemical structures and enhanced properties to replace the petroleum incumbents.

Epoxy resins are the most commonly employed thermosetting polymers, having high processing capability and a wide range of industrial applications such as protective coatings, insulating material for electrical and electronic components, adhesives, high-performance composites, encapsulants for semiconductors, concrete flooring, etc. [3]. The selection of epoxies for several fields of its application is based on their superior adhesion, excellent mechanical strength, permeability, high stiffness, outstanding

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chemical resistance properties [4]. Epoxy resins can be transformed into high-performance thermosetting resins via curing process wherein epoxy monomers are permanently crosslinked with suitable curing agents [5]. Amine based curing agents are of major importance among widely used and all known curing agents [6, 7]. In particular, aromatic amines as curing agents offer advantages of excellent chemical resistance, high-temperature stability, and good mechanical strength. Also, imide compounds end-capped with amines that contain aromatic groups have been used to impart flame resistance properties to the thermosetting resins [8, 9].

With the exhaustion of inherently finite fossil resources, the need for considering renewable resources in coating technologies is, therefore, obvious [10–13]. In recent times, few articles have reported the use of gum rosin as a scaffold material for synthesizing epoxy resins, providing an attractive alternative to prepare epoxy resins devoid of toxic and harmful Bisphenol-A which is a commercially used epoxy prepolymer [14]. Maleopimaric acid, a Diels-Alder adduct of rosin with maleic anhydride, has been used as a precursor for synthesizing bifunctional, trifunctional and multifunctional epoxy resins and curing agents that show great potential to replace some of the current petroleum-based products [15–18]. Several reports used ketone derivatives of rosin and condensed rosin acid-formaldehyde resins for preparing epoxy resins that show higher T_g value, enhanced thermal stability, and mechanical properties as compared to DGEBA [19–24]. Liu and coworkers [25–29] reported novel rosin-based imide-diacids and flexible anhydride type curing agents. A series of cured epoxy thermosets were prepared, and curing behavior was compared with commercial curing agents. They investigated thermal stability, tensile and mechanical properties of the rosin-based imide-diacids cured epoxy resins. The results demonstrated enhanced thermal performance, higher T_g values and superior mechanical properties of thermosetting resins attained by introducing rosin backbone in epoxy resins and curing agents. Moreover, modification of other various structurally versatile epoxy resins and curing agents with aromatic imides have been reported to show good fire-retardant properties [30, 31].

The present work focuses on the use of rigid hydrogenated phenanthrene moiety of gum rosin to synthesize both multifunctional bio-based epoxy resin as

well as the curing agent. In this study, rosin derived hyperbranched pentaerythritol based epoxy resin and rosin-based imidoamine curing agent was synthesized. The rigid rosin moiety is introduced in order to achieve higher glass transition, good thermal stability, and high mechanical strength of the cured epoxy thermosets. However, the fused rosin ketone structure used in the curing agent construction imparts brittleness to the resulting thermoset; hence, to overcome this issue, flexible diaminodiphenyl ether is incorporated into the dirosin-ketone structure via imide linkages. Furthermore, soft linear aliphatic ether segments present in pentaerythritol epoxy work as a flexible spacer between the huge imido-amine molecules in the crosslinked network structure. The pentaerythritol based epoxy resin was cured with rosin-based imidoamine, dimaleopimaryl ketone, and diaminodiphenyl ether curing agents. Their curing kinetics were studied and for comparison, trimethylol based epoxy resin (synthesized in our previous study [17]) was also cured with above mentioned curing agents. Thermal, mechanical and chemical resistance properties were also investigated. This study provides a novel method to develop fully bio-based high-performance thermosetting resin and further, the results demonstrate the feasibility of using it as a substitute for some existing petroleum-based resins and curing agents.

2. Materials and methods

2.1. Materials

Epoxy resin was synthesized using Gum rosin (WW grade, Midhills Rosin & Turpenes, India), maleic anhydride (99% pure, Lobachemie Pvt. Ltd., India), pentaerythritol (98% pure, Lobachemie Pvt. Ltd., India), *p*-toluenesulfonic acid (98% pure, Lobachemie Pvt. Ltd., India), epichlorohydrin L. R. grade (99% pure, Lobachemie Pvt. Ltd., India) and potassium hydroxide (85% pure, Avra Synthesis Pvt. Ltd, India). For synthesizing curing agents Diaminodiphenyl ether (98%, Alfa Aesar, UK), anhydrous sodium acetate (99% pure, CDH Pvt. Ltd, India), 2,4-Dichlorotoluene (98% pure, TCI Chemicals Pvt. Ltd, Japan) and propionic anhydride (98% pure, Sisco Research Laboratories Pvt. Ltd., India) were used. Solvents: acetic acid, xylene, toluene, dimethylformamide, ethyl acetate, petroleum ether, diethyl ether (Himedia Laboratories Pvt. Ltd., India) of reagent grade were used as received.

2.2. Synthesis of bio-based epoxy resin

2.2.1. Synthesis of MPA

In a three-necked 100 ml round bottom flask equipped with a mechanical stirrer, thermometer, and a reflux condenser, gum rosin (10 g) was added and heated to the melting range of 175–180 °C under N₂ atmosphere. The temperature was maintained for the next 3 hours to complete the isomerization of abietic acid to levopimaric acid and then the reaction mixture was cooled to 120 °C. After that maleic anhydride (2.35 g), acetic acid (30 ml) and *p*-toluenesulfonic acid (0.46 g) were added and refluxed for next 12 hours. Upon cooling, a yellow solid crude product was obtained which was further recrystallized with acetic acid to give white crystals of pure MPA. Yield 92%.

2.2.2. Synthesis of esterified adduct of MPA with pentaerythritol (PEMPA)

To a 100 ml three-necked round bottom flask fitted with mechanical stirrer, Dean and stark apparatus and thermometer, MPA (10 g), Pentaerythritol (6.4 g), xylene (10 ml) and *p*-TSA (1 wt% of total weight of reactants) was charged. The reaction mixture was refluxed until 6 moles of water were collected. A light yellow solid product was obtained and washed with hot water to remove unreacted pentaerythritol. Yield 91%.

2.2.3. Synthesis of epoxy resin (PEMPAE)

30 g PEMPAA and 220 ml DMSO were mixed at 24 °C in a reaction kettle equipped with a mechanical stirrer, water bath, and reflux condenser. After PEMPAA was dissolved, 116 g of KOH was added to the reaction mixture and the temperature was maintained to 15–20 °C using ice in a water bath. To this mixture, 272 ml of epichlorohydrin was added dropwise in 1.5 hours and continued stirring for the next 16 hours. The reaction product was then extracted with equal amounts of dichloromethane and water mixture. After separating the non-aqueous layer, excess of Dichloromethane was distilled off under reduced pressure and the light yellow colored epoxy resin was obtained.

2.3. Synthesis of bio-based imidoamine curing agent

2.3.1. Synthesis of ketone derivative of MPA (DMPK)

Dimaleopimaryl ketone (DMPK) was synthesized by acid-catalyzed dehydrodecarboxylation reaction

of MPA. A mixture of 101 g of MPA and 50 ml of toluene was charged to a reaction vessel fitted with a mechanical stirrer, Dean and Stark apparatus, thermometer, and an N₂ inlet. The reaction mixture was heated to 112 °C and refluxed for 30 mins. 1 g of *p*-TSA was added and refluxed for the next 15 mins. After collection of about 0.5 ml of water in dean-stark, the reaction temperature was slowly raised to 200 °C for the next 2.5 hours with the gradual removal of toluene from the reaction mixture. At this instant, the removal of byproducts (CO₂ and water) was observed. The reaction was completed during the next 30 mins. A brownish colored solid crude product was obtained which was purified by dissolving in diethyl ether and then after filtration, precipitation was done with petroleum ether. Yield 52%.

2.3.2. Synthesis of imidoamine-ether-dimerketone (IAEDK) curing agent

Imidoamine curing agent was synthesized by reacting one mole of DMPK with excess (2.5 mol) of diaminodiphenylether (DDE). Firstly, a solution of 10 g of DDE in 50 ml of 2,4-dichlorotoluene was added to a 100 ml three-neck round bottom flask fitted with a stirrer, Liebig condenser, and thermometer. The solution was heated to boiling and then a hot solution of 15.4 g of DMPK in 150 ml of 2,4-dichlorotoluene was added dropwise in next 15 mins during constant boiling. The contents were refluxed for the next 5 hours. The solvent was then removed by the rotary evaporator. Dark brown colored residual crude was obtained which was purified in ethyl acetate and dried. Yield 58%.

2.4. Curing procedure

Epoxy resins PEMPAAE and TMPAAE were cured with imidoamine curing agent (IAEDK), DMPK and DDE. Six different samples were prepared by mixing the epoxy resin and curing agent in a 1:1 equivalent ratio in a beaker and dissolved in a small amount of acetone in order to achieve a homogenous mixture. The mixture was stirred for 30 mins at room temperature and then the solvent was removed in a vacuum oven at 50 °C for 3 hours. After that, the mixture was transferred into a mold with dimensions 100×50×5 mm. The curing was done under constant pressure in a compression molding machine at 90 °C for 1 h, 120 °C for 2 h, 150 °C for 2 h. The samples were cooled to room temperature and removed carefully from the mold. The resulting sheet of the cured sample

was cut into rectangular strips of 100×10×5 mm size for testing the mechanical properties.

2.5. Characterizations

The structural characterization of all the synthesized compounds was done using FTIR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. FTIR spectra were recorded in KBr pellets using Perkin Elmer L1600312 FTIR spectrometer in range 4000–500 cm⁻¹. ¹H-NMR and ¹³C-NMR spectra were measured on Jeol India JNM ECX -500 spectrometer in CDCl₃ solvent. The molecular weight of bio-based epoxy resin and imidoamine curing agent was determined using Perkin Elmer turbo matrix-40 Gel Permeation Chromatograph. Tetrahydrofuran (THF) was used as a mobile and stationary phase in GPC. The curing behavior of epoxy resins with synthesized and commercial curing agents was studied by DSC. For this, SDT Q600 V20.9 Build 20 Differential Scanning Calorimeter was used and the scans were recorded by taking 2 mg (approx.) of the sample into alumina crucible from 20 to 250 °C dynamically with a heating rate of 10 °C/min. Thermogravimetric analysis experiments were conducted using EXSTAR TG/DTA 6300 under nitrogen atmosphere at a constant heating rate of 10 °C/min. The mechanical analysis of cured samples was carried out to study the tensile strength, compressive strength and flexural properties using Hounsefield-25KN universal testing machine at a strain rate of 2 mm/min.

The chemical resistance of the cured epoxy resins was also evaluated according to ASTM method as reported in a previous study [23] using mild steel specimens (15×10 cm), one side of which is coated with coal tar epoxy primer and another side with an epoxy resin containing amine hardener having thickness 250±10 μm via hand layup method and was cured. These specimens were then immersed in 1M NaOH, 1M HCl, and 1M NaCl solutions for 90 days at room temperature. The chemical resistance was determined by analysis based on weight loss of the cured resin coated on steel specimens using Equation (1):

$$\text{Weight loss [\%]} = \frac{W_i - W_f}{W_i} \quad (1)$$

where W_i is the weight of the dry sample before immersion and W_f is the weight of the dry sample after immersion. Morphological changes on the surface of the tested side of the specimen due to chemical

exposure were observed using the JSM-6610 Scanning electron microscope.

3. Results and discussion

Gum rosin consists of 90% rosin acids (pimaric and abietic type) and 10% neutral compounds. Rosin acids show chemical reactivity due to the presence of two main functionalities: conjugated double bonds and monocarboxylic acid groups. Out of eight closely related rosin acid isomers, only levopimaric acid possesses the homoannular double bonds for Diels-Alder cycloaddition. However, the other rosin acids can be isomerized to levopimaric acid by heating at elevated temperatures which can further be modified with maleic anhydride to get Diels-Alder adduct (MPA). To introduce flexibility and hydroxyl functionality, this adduct was further reacted with pentaerythritol, an appropriate candidate due to its aliphatic hydrocarbon chain and four hydroxyl groups. The hydroxyl groups were epoxidized to synthesize multifunctional epoxy resin. Hence, a non-glycidyl ester of pentaerythritol modified MPA based epoxy resin was prepared. In order to obtain a high-performance epoxy thermoset, a rosin-based crosslinker was also prepared. This amine type rosin crosslinker in conjunction with imide units was synthesized by firstly dehydrodecarboxylating MPA to get dimaleopimaryl ketone which was further reacted with diaminodiphenyl ether to form an imidoamine. Thus, epoxy resin and crosslinker were mixed together in the stoichiometric ratio to yield thermosetting resin with enhanced mechanical and thermal strength.

3.1. Synthesis and characterization

Figure 1 and 2 depicts the synthesis of pentaerythritol rosin epoxy resin (PEMPAE) and imidoamine (IAEDK) curing agent, respectively. The chemical structure of PEMPAE epoxy resin was confirmed by FTIR, ¹H-NMR, and ¹³C-NMR techniques. Figure 4a shows FTIR spectra for PEMPAE epoxy resin and its precursors MPA and PEMPA. The FTIR spectrum of MPA shows a broad absorption peak in range 3300–3600 cm⁻¹ for the carboxylic –OH stretching, two stretching bands at 1828 and 1766 cm⁻¹ for anhydride stretching and a peak at 1678 cm⁻¹ for C=O of carboxylic acid which confirms the Diels-Alder adduct formation. In the FTIR spectrum of PEMPA, peaks at 1700 and 1730 cm⁻¹ due to the carbonyl of acid and ester appeared and the peaks due to anhydride

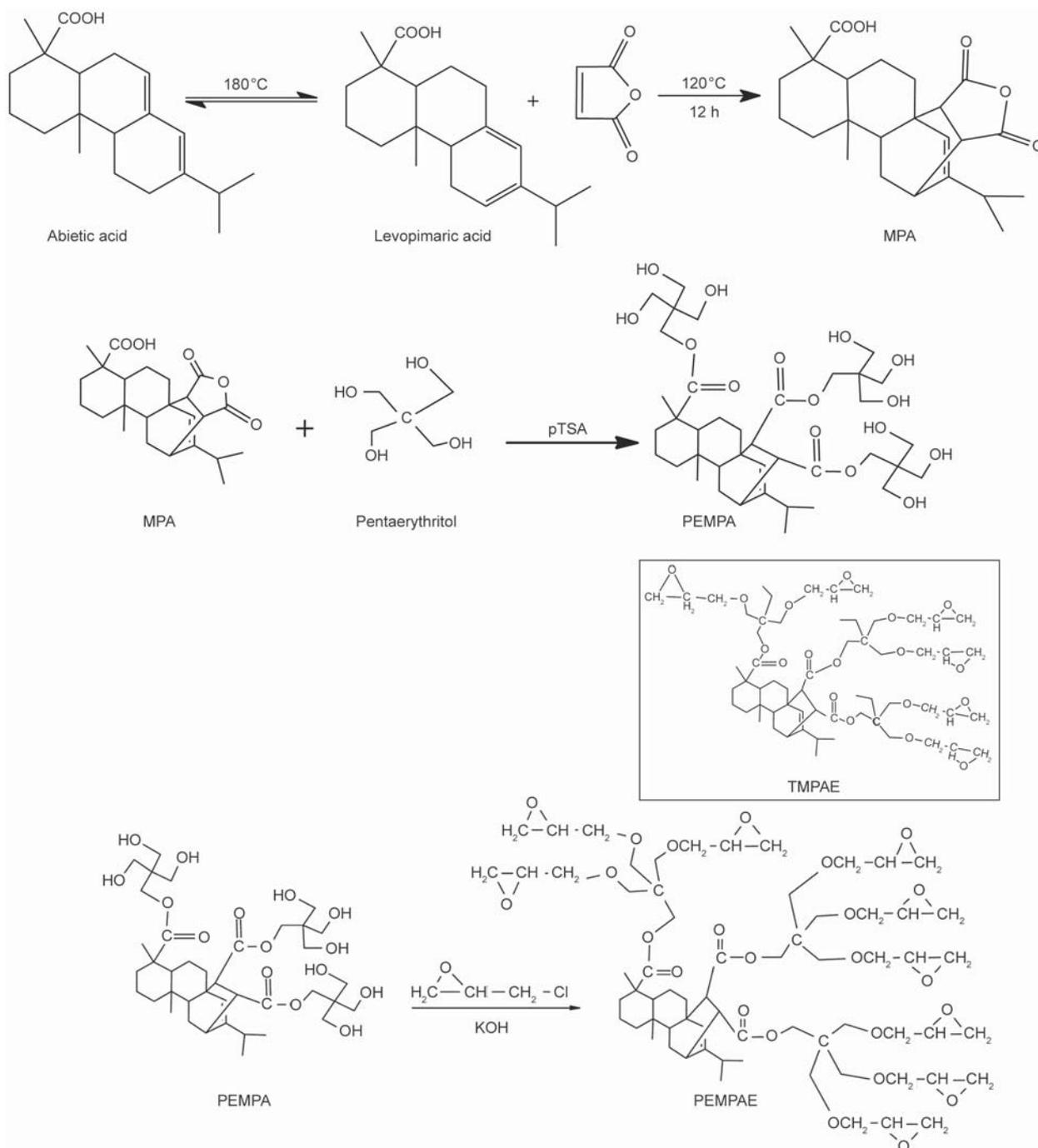


Figure 1. Synthetic route for PEMP AE epoxy resin.

disappeared which confirms the esterification of MPA with pentaerythritol. For epoxy resin PEMP AE, three characteristic bands for C–O stretching: symmetric at 1240 cm^{-1} and asymmetric at 887 and 821 cm^{-1} were observed. Figure 5 shows the $^1\text{H-NMR}$ spectra of MPA (Figure 5a), PEMP AE (Figure 5b) and PEMP AE (Figure 5c). For MPA, the signal at 5.5 ppm is due to the proton (3) at unsaturated carbon, the signal at 11.6 ppm is due to carboxylic acid proton (6) and other peaks were also identified. The $^1\text{H-NMR}$ of PEMP AE shows signal due to hydroxyl

protons at 3.6–4.2 ppm confirming esterification of MPA with pentaerythritol. The peak at 5.5 ppm is retained which shows that the MPA structure remains intact during the esterification reaction. The structure of epoxy resin PEMP AE was confirmed by $^1\text{H-NMR}$ spectrum (Figure 5c) as the peak assigned to hydroxyl protons was not observed in the range 3.6–4.02 ppm. The presence of signals at 2.6 and 2.8 ppm was due to protons 4 and 5 of the oxirane ring, respectively. The peak observed at 3.1 ppm is attributed to proton (1) and a multiplet at 3.3–3.8 ppm is

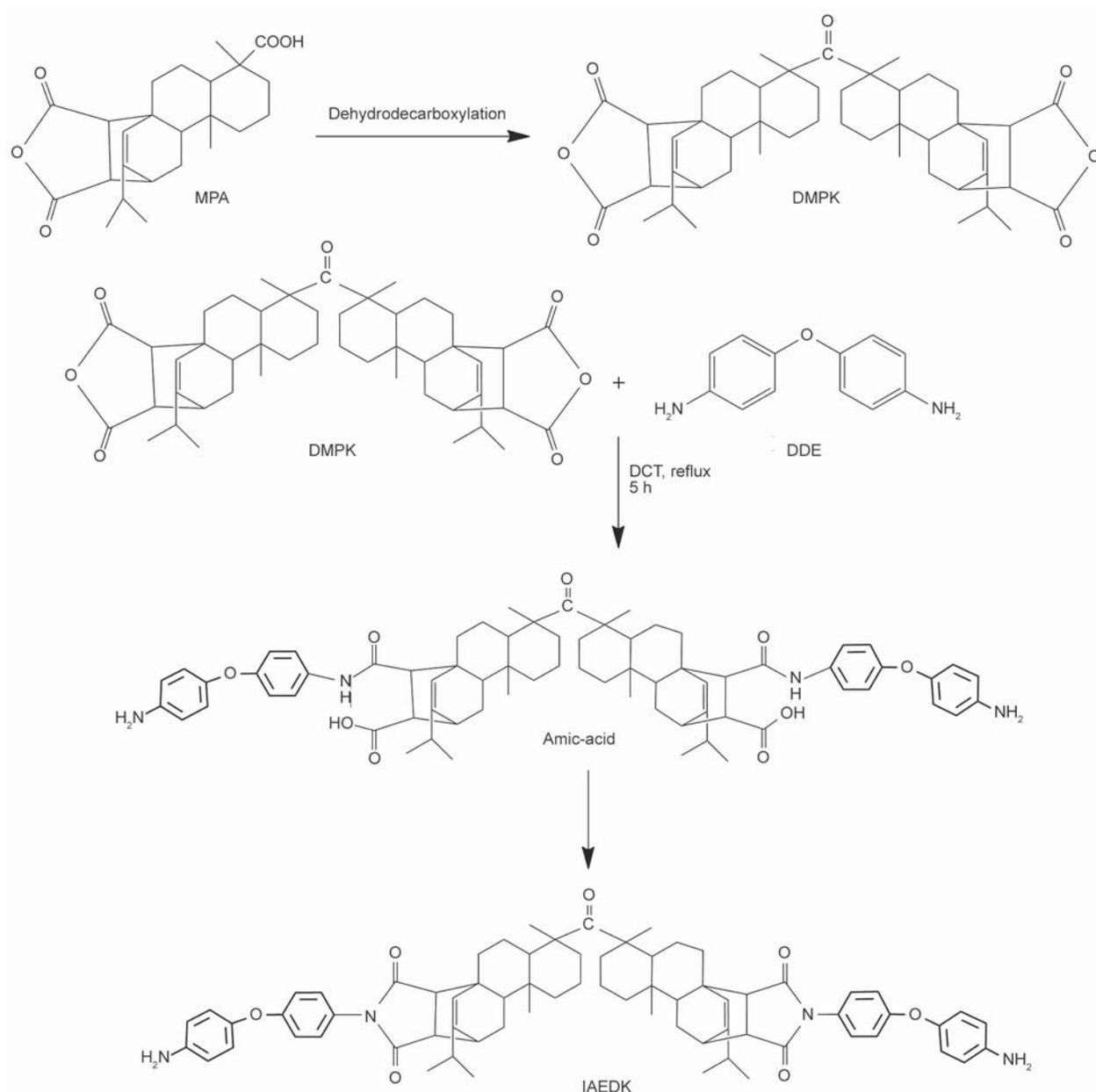


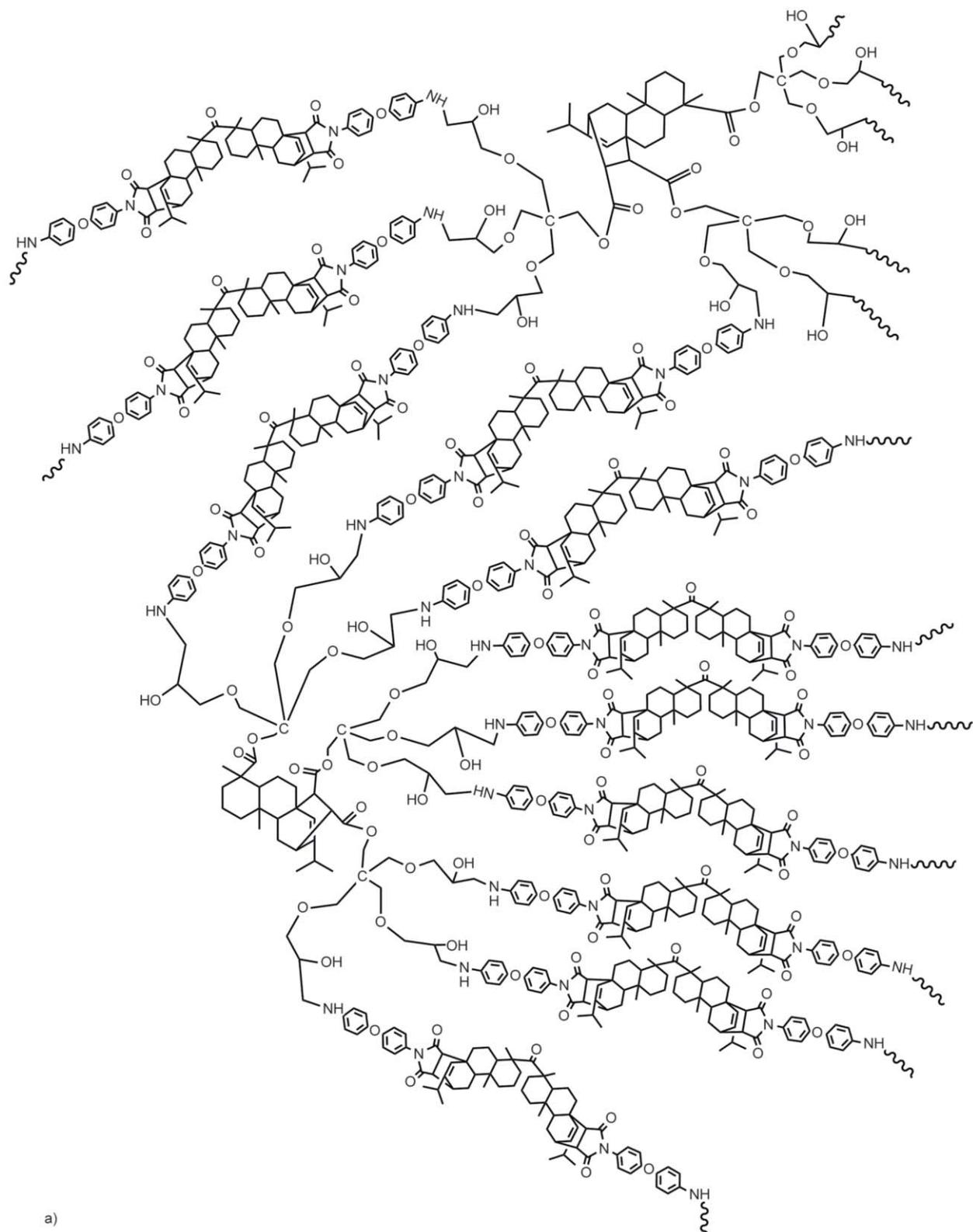
Figure 2. Synthetic route for IAEDK curing agent.

assigned to proton (2). Figure 6a displays the ^{13}C -NMR spectrum of PEMPAE wherein the signals were observed at 180, 175 and 173 ppm for carbonyl carbons of the ester groups at 5, 6 and 7, respectively. This confirms the esterification of the carboxylic acid group. The resonance signals observed at 121 and 130 ppm are assigned to unsaturated carbons 3 and 4, respectively. The peaks due to carbon 1, 2 and 8 of epoxide group are observed at 44, 51 and 72 ppm respectively, which proves the epoxidation of PEMPA. The chemical structure of the rosin modified imidoamine curing agent (IAEDK) was also confirmed by FTIR, ^1H -NMR, and ^{13}C -NMR. The FTIR spectrum (Figure 4b) of DMPK shows the disappearance of peak at $3300\text{--}3600\text{ cm}^{-1}$ for the carboxylic $-\text{OH}$

present in MPA confirming the dimerization of MPA to DMPK. In the FTIR of IAEDK, the appearance of a peak at 1692 cm^{-1} for the $\text{C}=\text{O}$ of amide and disappearance of peaks due to anhydride $\text{C}=\text{O}$ stretching vibrations can be observed which confirms the imide bond formation. Also, two characteristic peaks at 3358 and 3325 cm^{-1} show the presence of $-\text{NH}_2$ group. In the ^1H -NMR of DMPK (Figure 5d), the disappearance of the signal at 11.6 ppm for carboxylic acid proton in MPA confirms the dimerization reaction. Figure 5e shows the ^1H -NMR spectrum of IAEDK wherein the peak at 5.5 ppm is due to the proton (1) at unsaturated carbon and the signal at 4.1 ppm attributes to the aromatic $-\text{NH}_2$ protons (2). The protons (5) and (6) were characterized by signals

which appeared at 3.1 and 2.9 ppm, respectively. The resonance signals observed in range 6.6–7.3 ppm corresponds to the aromatic protons of benzene ring present in the imidoamine moiety. The ^{13}C -NMR spectrum of imidoamine crosslinker is shown in Figure 6b. The signals due to the carbonyl carbon of ketone and cyclic imide can be observed at 185 ppm (carbon 1),

178 ppm (carbon 2) and 176 ppm (carbon 3). The unsaturated carbons 8 and 6 show signals at 128 and 149 ppm, respectively. The aromatic carbon 7 bonded with $-\text{NH}_2$ shows a peak at 142 ppm and carbon 4 involved in ether linkage appears at 158 ppm. The molecular weight determined by GPC and melting points of synthesized products are shown in



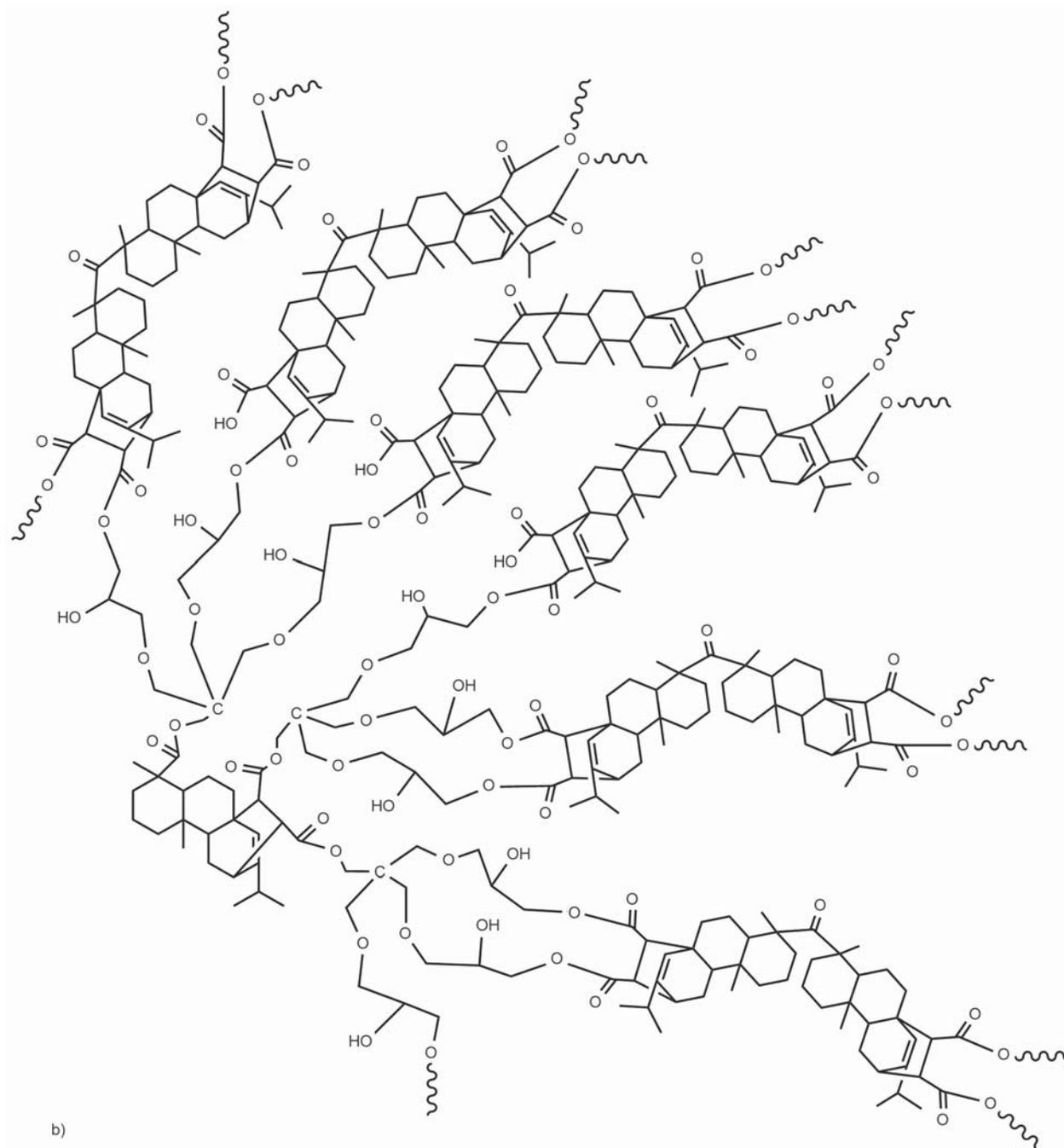


Figure 3. Proposed crosslinking of (a) PEMPAE epoxy resin with IAEDK and (b) PEMPAE epoxy resin with DMPK curing agents.

Table 1 and the typical GPC graph for PEMPAE epoxy resin is presented in Figure 7a giving the molecular weight of 1277.5 g/mol. The single peak appeared in the GPC graph, which shows the absence of side reactions during synthesis. The molecular weights of PEMPA adduct and PEMPAE epoxy resin were also determined using $^1\text{H-NMR}$ analysis. In order to determine the molecular weight of the epoxy, the hydroxyl functionality in PEMPA was known by the acetic anhydride/pyridine method [32]. The hydroxyl value obtained showed the presence of

9 hydroxyl groups. These values were also calculated from the $^1\text{H-NMR}$ data by relating the integration of hydroxyl protons (proton 1) to that of the double bond proton (proton 3) (Figure 5b). Thus, the hydroxyl functionality was found to be 9 (11.26/ 1.25), which matches that obtained from a chemical titration procedure. This proves the formation of PEMPA molecule. The molecular weight was calculated to be 772.92 g/mol according to the chemical structure of PEMPA which is similar to the value obtained from GPC graph.

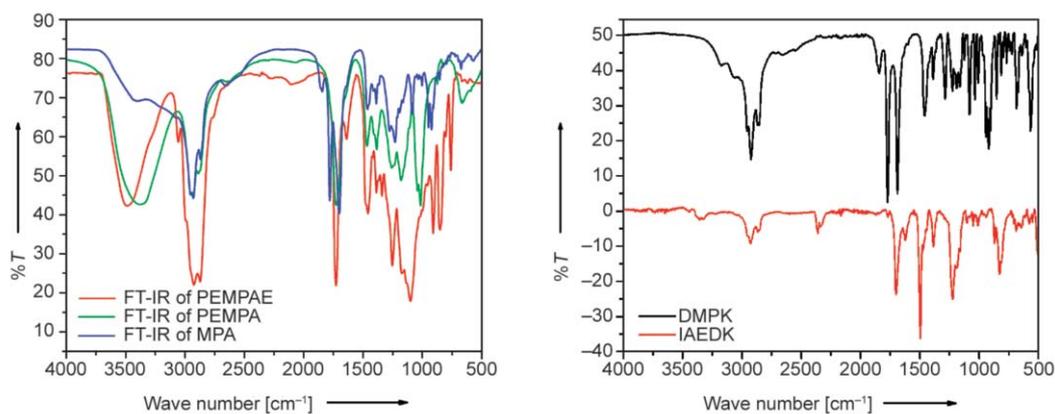
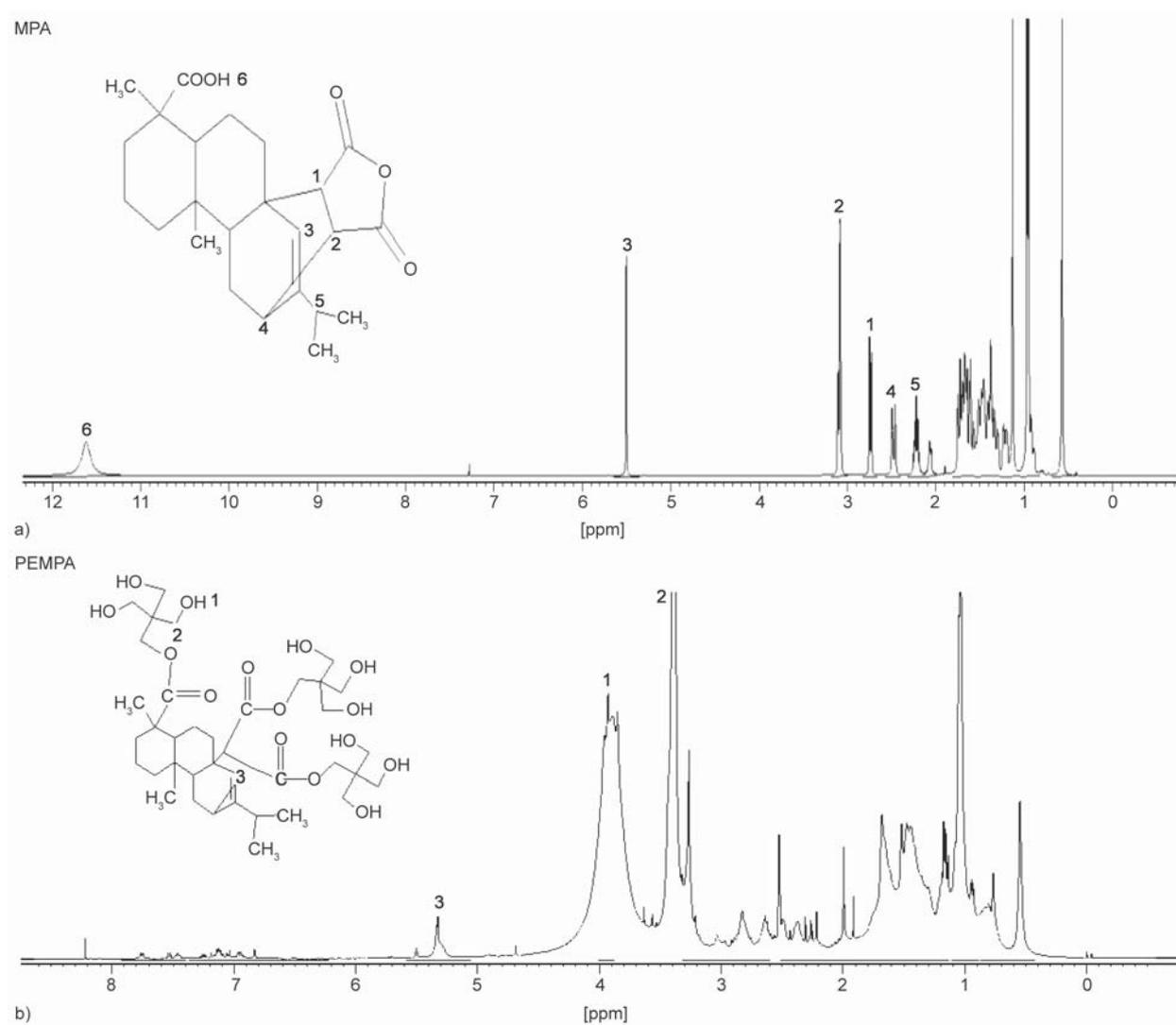


Figure 4. FTIR spectra of (a) MPA, PEMPA and PEMPAE (b) DMPK and IAEDK.

Similarly, the epoxide equivalent weight for PEMPAE epoxy resin was determined to be 151.23 g/eq by pyridinium chloride method [33]. The epoxy functionality for PEMPAE was calculated by the formula, $E = 1000/EEW$, which comes out to be 6.6 eq./kg. The molecular weight formula can be given as

$(772.92 + 56F)$, where 772.92 is the molecular weight of PEMPA, 56 is the molecular weight of one epoxy group and F is the total epoxy functionality per molecule. Therefore, the epoxy functionality per molecule was calculated from the epoxy value (E) determined by titration method using Equation (2):



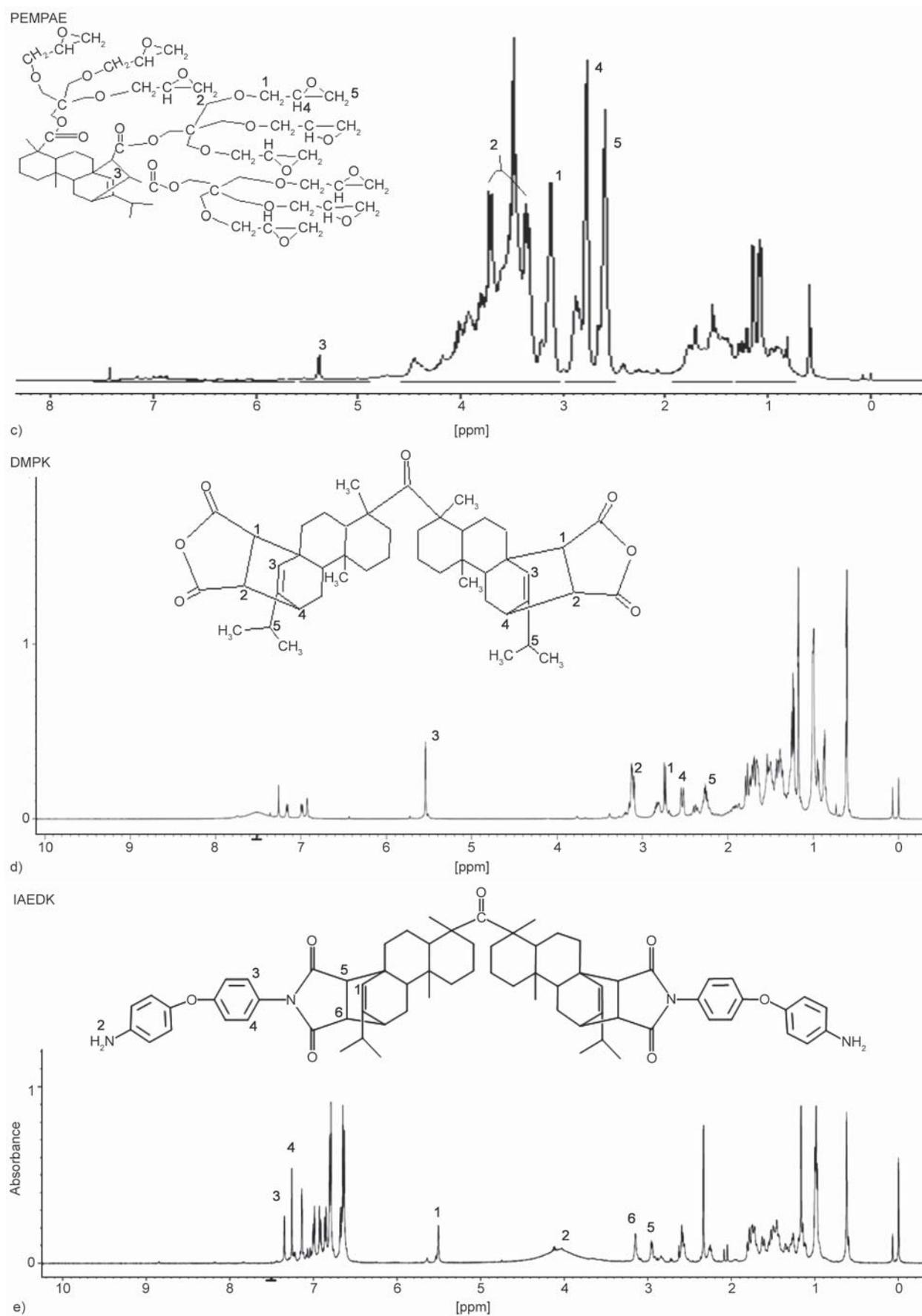


Figure 5. ^1H NMR spectra of (a) MPA, (b) PEMPA, (c) PEMPAE, (d) DMPK and (e) IAEDK.

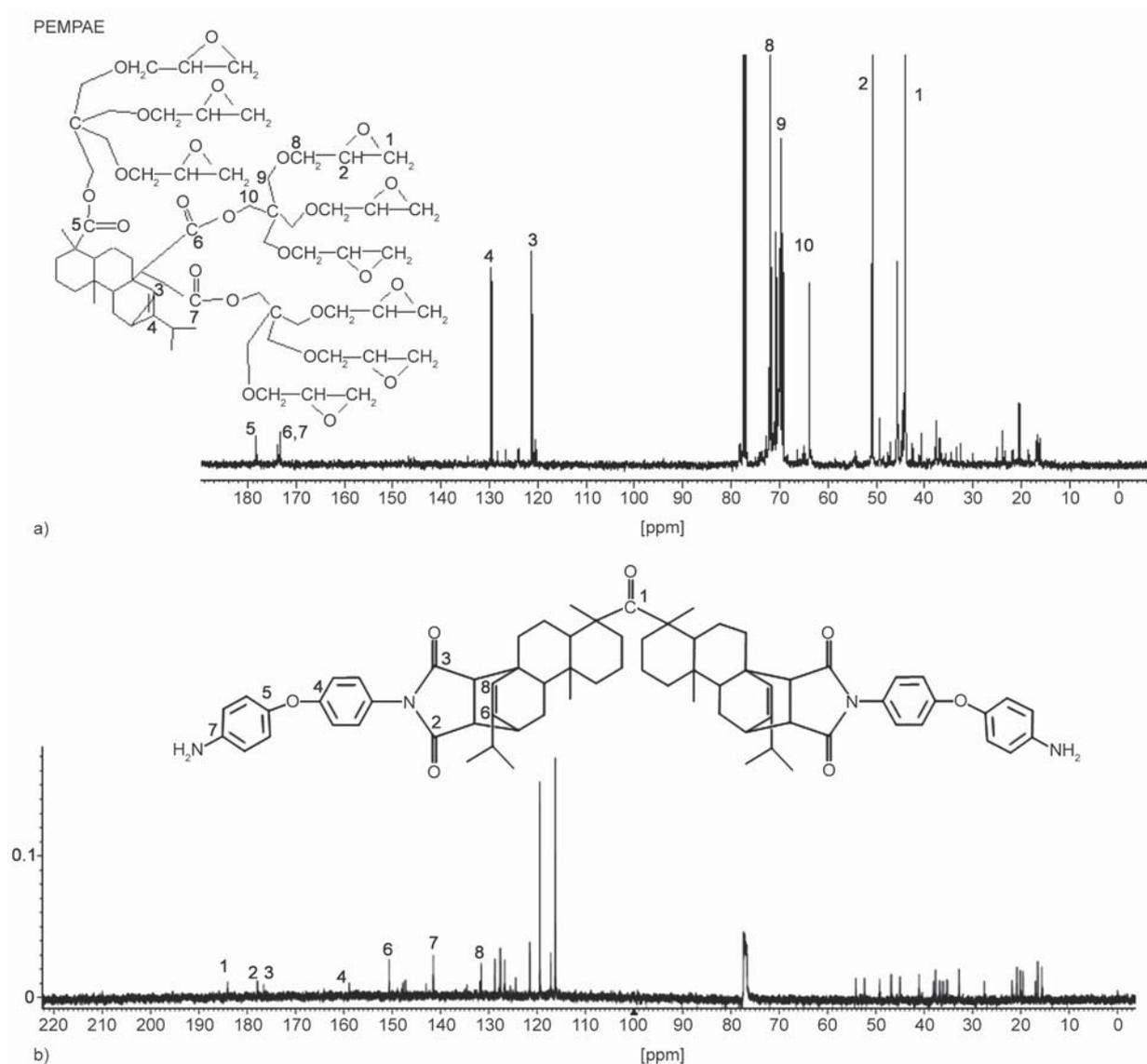


Figure 6. ^{13}C NMR spectra of (a) PEMPAAE epoxy resin and (b) IAEDK curing agent.

$$F = \frac{772.92 \cdot E}{1000 - (56 \cdot E)} = \frac{772.92 \cdot 6.6}{1000 - (56 \cdot 6.6)} = 8.09 \approx 8.1 \quad (2)$$

The epoxy functionality was also calculated via ^1H -NMR analysis. It was determined from the ratio of integration of epoxy protons (proton **5**) to the integration of double bond proton (proton **3**) (Figure 5c). Thus, the number of epoxy groups is given by, $F = (2.09/0.24) = 8.7$, which comes to be almost equal to the value determined by the titration method. The molecular weight can be determined using the formula: Mol. Wt. = $(772.92 + 56F) = (772.92 + 56 \cdot 8.7) = 1260.12$ g/mol, which is comparable to the value determined by GPC graph.

The typical GPC graph for synthesized curing agent IAEDK is shown in Figure 7b. The molecular weight of 1056.2 g/mol and polydispersity (PDI) of 1.06 was

Table 1. GPC determined molecular weights and melting points of synthesized products.

Samples	Weight average molecular weight, \bar{M}_w [g/mol]		Melting point [°C]
	Experimental values	Theoretical values	
MPA	398.67	400.51	232
PEMPA	775.40	772.92	120
PEMPAAE	1277.50	1242.88	–
DMPK	796.40	739.01	130
IAEDK	1056.20	1103.49	145

obtained from the graph. The GPC graph displays a single narrow peak which depicts the absence of side reactions. The molecular weight for imidoamine curing agent was also determined as 1104 g/mol according to its chemical structure which is comparable to the value determined by GPC. The amine equivalent

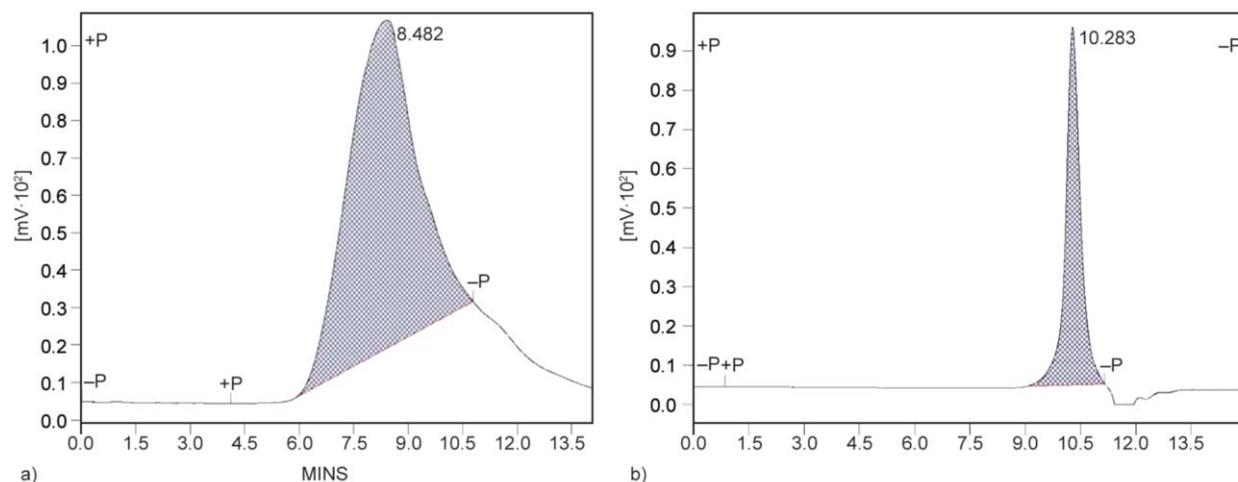


Figure 7. GPC of (a) PEMPAE and (b) IAEDK.

Table 2. Composition of different epoxy cured samples.

S.No.	Epoxy	Curing agent	Sample Id	Weight ratio (Curing agent: epoxy)
1.	PEMPAE	IAEDK	PDA	3.3:1
2.	PEMPAE	DMPK	PDK	2.3:1
3.	PEMPAE	DDE	PDE	0.6:1
4.	TMPAE	IAEDK	TDA	2.7:1
5.	TMPAE	DMPK	TDK	1.9:1
6.	TMPAE	DDE	TDE	0.5:1

weight (552 g/eq.) was also calculated for the IAEDK curing agent by taking a ratio of molecular weight to the number of available hydrogens per molecule. The epoxide equivalent and amine equivalent values were used for computing the stoichiometry of epoxy and curing agent for the curing reaction. Table 2 shows the appropriate curing agent to the epoxy weight ratio for six different samples using two epoxies (PEMPAE & TMPAE) and three curing agents (IAEDK, DMPK & DDE).

3.2. Curing studies

The curing behavior of the epoxy resins PEMPAE and TMPAE with different curing agents IAEDK,

DMPK and DDE were carried out using Differential Scanning Calorimeter at a programmed heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Figure 8a shows a typical DSC (exo up) curve for PEMPAE epoxy resin with IAEDK curing agent in the temperature range $70\text{--}225\text{ }^{\circ}\text{C}$. The DSC curing temperatures and energy corresponding to exotherms (ΔH) for all the cured epoxy systems are summarized in Table 3. The onset and peak temperatures depicted from the DSC curves indicate the reactivity of the curing agents with epoxy resins throughout the curing reactions, i.e. lower values of onset exothermic temperature shows more reactivity of the curing agent towards the epoxy resin. The exothermic transition for the sample PEMPAE-IAEDK (PDA) ensure lowest curing temperature with $72\text{ }^{\circ}\text{C}$ onset, $117\text{ }^{\circ}\text{C}$ peak, and $167\text{ }^{\circ}\text{C}$ endset temperatures. This signifies that the imidoamine curing agent offers the highest reactivity towards epoxy resin among all the three curatives. The amine group reacts with epoxide ring via nucleophilic addition reaction. Figure 3a shows the proposed network structure formed by crosslinking of imidoamine curing agent with PEMPAE epoxy resin. The reason for the highest reactivity of imidoamine curing agent must

Table 3. DSC results of cured epoxy resin samples.

Name of sample	Onset temperature [$^{\circ}\text{C}$]	Peak temperature [$^{\circ}\text{C}$]	Endset temperature [$^{\circ}\text{C}$]	Enthalpy change, ΔH [J/g]
PEMPAE+IAEDK	72	117	167	21.60
PEMPAE+DMPK	112	172	224	25.30
PEMPAE+DDE	80	140	185	33.40
TMPAE+IAEDK	96	118	134	20.20
TMPAE+DMPK	120	180	220	16.51
TMPAE+DDE	80	135	185	24.80

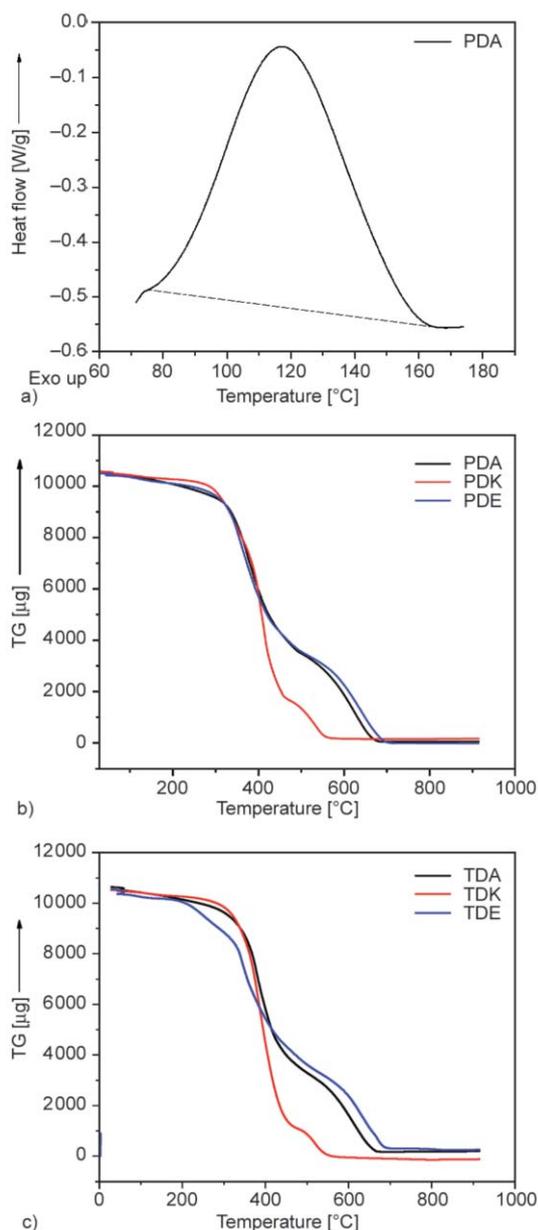


Figure 8. (a) DSC Scan for curing of rosin epoxy resin PEMPAAE with IAEDK curing agent (b) TGA curves of epoxy PEMPAAE cured with different curing agents and (c) TGA curves of epoxy TMPAAE cured with different curing agents.

be the increased nucleophilicity of amine groups due to the introduction of rosin moiety which showed an electron-donating effect. Moreover, the cycloaliphatic phenanthrene ring reduces the aromaticity of imidoamine curing agent hereby lowering its melting temperature than that of aromatic DDE curing agent. Chiu *et al.* [34] found that the aromatic amine curing agents shows high-temperature curing than that of aliphatic amine curing agents owing to their chemical structures and electron-withdrawing properties. Thus, less aromatic IAEDK shows more reactivity

and low temperature curing towards rosin epoxy resins. For commercial curing agent DDE, curing with rosin epoxy resins starts at 80°C which is higher than imidoamine curing agent. Burkanudeen and Ramesh [35] reported the DSC curing study of DGEBA (commercial epoxy resin) with DDE that exhibited curing onset temperature 140°C and peak temperature 159°C. These results are much higher than that obtained by rosin-based epoxy resins PEMPAAE and TMPAAE with DDE, an observation that shows higher reactivity of rosin-based epoxy resins with DDE as compared to commercial DGEBA epoxy resin. Furthermore, anhydride curing agent DMPK exhibits a higher curing temperature than amine-based curing agents. An anhydride group reacts with two epoxy groups to give hydroxyl diester which further reacts with excess epoxy groups to form a crosslinked polyester network [26]. Figure 3b shows proposed crosslinked network structure for DMPK curing agent with PEMPAAE epoxy resin. This homopolymerization of epoxy results in high temperature curing exotherm for epoxy-anhydride curing system. Also, the Pentaerythritol based epoxy resin showed low temperature curing *i.e.* higher reactivity than trimethylol based epoxy resin because of the greater number of epoxy groups in PEMPAAE. DTA run was carried out on the cured samples in order to check for residual curing. The absence of residual curing exotherm indicated the samples to be completely cured. Additionally, the enthalpy of the reaction (ΔH) is also observed to be lower for the imidoamine and DMPK cured epoxy samples than the DDE cured epoxy which signifies the higher degree of curing or crosslinking in epoxy resins cured with rosin-based curing agents [36].

3.3. Thermal behavior of cured epoxy systems

The study of thermal degradation of epoxy thermosets is significant in analyzing the use temperature range for the epoxy system. For this investigation, TGA is considered to be the most convenient and commonly employed technique for isothermally cured epoxy systems. Table 4 summarizes the relative thermal stability for different samples with respect to initial decomposition temperature (IDT), the temperature at which maximum decomposition occurs (T_{max}), final decomposition temperature (FDT), weight loss [%] at maximum decomposition temperature, activation energies, temperatures at which 5, 10, 20% weight loss occurs and char yield [%] at 600°C. Figure 8b

Table 4. TGA studies of various cured epoxy compounds.

Name of sample	IDT [°C]	T_{max} [°C]	FDT [°C]	Temperatures at weight loss %			Weight loss at T_{max} [%]	Activation energy, ΔE [KJ/mol]	Char yield at 600°C [%]
				5%	10%	20%			
PEMPAE+IAEDK	246	379	524	263	304	350	66	89.8	15.2
PEMPAE+DMPK	222	405	484	279	313	348	50	98.0	0.5
PEMPAE+DDE	174	354	516	245	313	348	77	73.1	22.0
TMPAE+ IAEDK	230	378	520	246	305	355	68	86.0	17.7
TMPAE+DMPK	210	388	476	281	322	352	52	96.0	1.5
TMPAE+DDE	154	343	468	202	250	323	73	59.8	21.6

and 8c shows the TGA curves for epoxy resins PEMPAE and TMPAE cured with IAEDK, DMPK, and DDE curing agents, respectively. The epoxies cured with IAEDK exhibits maximum thermal stability with IDT 246 °C and T_{max} 349 °C for PDA and IDT 230 °C and T_{max} 378 °C for TDA. The reason may be attributed to three dimensional crosslinked network structure established by multifunctional epoxy resin with diamine curing agent and also due to high ordered packing structure formed by planar phenanthrene and rigid phenyl rings present in curing agent moiety. El-Ghazawy *et al.* [21] have reported a fully rosin-based system in which tetraglycidyl epoxy synthesized by epoxidation of dipimaryl ketone (DMPK) was cured with synthesized diacid crosslinker that shows high thermal stability than that of DGEBA epoxy system cured with commercial diamine crosslinker. They found that the rosin epoxy system was stable till 360 °C and this high stability is due to the well-ordered crosslinking and analogy in structures of both epoxy and curing agent. Furthermore, the incorporation of imide units into the curing agent molecule greatly influenced the thermal performance of the cured epoxy system. Liu *et al.* [25] observed significantly improved thermal stability of epoxy-diacid system via imide units present in the rosin derived diacid crosslinker. The epoxy samples cured with anhydride type DMPK curing agent showed thermal stability as good as imidoamine curing agent and a slow degradation rate at an early phase of decomposition was found but a rapid thermal decomposition was observed as the scanning temperature exceeds 400 °C. The samples cured with DDE commercial curing agent come out to be thermally least stable and shows IDT 174 °C and T_{max} 354 °C. These values were compared to the previously reported study of Patel *et al.* [37] where the authors used DGEBA, phenyl based epoxy resin with DDE that exhibited IDT 148 °C and 10% weight loss temperature of 240 °C that shows lesser thermal stability

of commercial DGEBA/DDE as compared to rosin-based PEMPAE epoxy resin. Also, in case of pentaerythritol based epoxy resin, higher T_{max} values were observed which may be attributed to the greater epoxy functionality producing highly crosslinked network than trimethylol based epoxy resin. These results show that rosin derived imidoamine and DMPK curing agents give rise to more stable epoxy thermosets as compared to commercial curing agents. The study shows that the thermal stability of cured resins depends upon the structure of curing agents and the crosslinking sites of two component epoxy matrix.

The activation energy of the thermal degradation reaction was calculated from TGA data by a method independent of heating rates and sample size reported by Dharwadkar *et al.* [38]. The equation for E_a is given by Equation (3):

$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E_a \cdot 100\theta}{RT_i^2(T_f - T_i)} + C \quad (3)$$

where α is degrading fraction; T_i is inception temperature; T_f is inflection temperature; θ is the difference of maximum temperature and temperature under consideration; R is gas constant; C is constant. E_a is evaluated by plotting $\ln[\ln(1 - \alpha)^{-1}]$ vs θ giving a straight line with slope m (Equation (4)):

$$m = \frac{E_a \cdot 100}{RT_i^2(T_f - T_i)} \quad (4)$$

Thus activation energies of decomposition for all the samples were evaluated by Equations (3) and (4) and listed in Table 4. It can be seen that the epoxies cured with rosin-based curing agents showed a greater value of activation energy than that of the commercial one. Also, anhydride type curing agent (DMPK) showed the highest value of E_a among all due to the strong diester bonds which tend to enhance the thermal stability.

3.4. Mechanical analysis of cured epoxy systems

Mechanical properties of cured epoxy systems entirely depend upon the chemical structures of both epoxy and hardener and their degree of crosslinking. Keeping this in view, the two-component coating system was designed to generate cured resin with high mechanical properties. For studying the mechanical behavior of cured epoxy resins, compression, flexural and tensile tests were performed and results have been summarized in Table 5. The data illustrates that epoxy cured with rosin curing agents exhibited higher mechanical strength as compared to commercial DDE. Furthermore, imidoamine cured epoxy offered best outcomes for tensile, compression and flexural strength which must be owing to the strong polar interactions of imide, esters and carbonyl groups present in the crosslinked network which tends to reduce the chain mobility and resist the matrix deformation. In the case of DMPK cured resin, mechanical strength values are lesser than the former because of the brittle nature of the dimerized rosin moiety present in the crosslinker. Moreover, pentaerythritol based epoxy system showed better mechanical behavior than trimethylol one that reflects higher

crosslinking and amplified polymer chain interactions due to more epoxy functionality of PEMPAE resin. The study shows that the rosin-based epoxy and curing agent system can be a substitute for the incumbent petroleum-based systems.

3.5. Chemical resistance of cured epoxy systems

Chemical resistance of the cured epoxy systems was assessed by subjecting the cured epoxy coated steel specimens to the chemical environment of the acid, base, and salt in terms of % weight loss. For this study, specimens were immersed in 1M HCl, 1M NaCl and 1M NaOH aqueous solutions for 90 days and weight loss was noted after a period of 30, 60 and 90 days of immersion. Table 6 shows the results of chemical resistance for the epoxy cured samples which demonstrate that imidoamine cured epoxy sample is the most resistant to the chemical environment. The existence of a highly crosslinked network must be the ultimate factor that prevents the cured sample from solvent attack. Also, the presence of hydrogen bonding and polar groups in the polymer chains greatly affects the diffusion of solvent molecules. The high chemical resistance in the case of imidoamine cured sample indicates the high degree of crosslinking of imidoamine curing agent with pentaerythritol based epoxy resin [39]. Atta *et al.* [23] performed chemical resistance tests on epoxy resins cured with amine curing agents and found that the rosin-based epoxy binders show more resistance to acidic and alkaline solutions due to highly crosslinked networks which reduces its environmental exposure. Likewise, the DMPK cured resins also exhibited good solvent resistance as compared to commercial DDE cured

Table 5. Mechanical tests of cured epoxy samples.

Name of sample	Compression strength [MPa]	Flexural strength [MPa]	Tensile strength [MPa]
PEMPAE+IAEDK	80.7	82.8	28.1
PEMPAE+DMPK	37.8	46.8	16.4
PEMPAE+DDE	20.2	35.7	13.5
TMPAE+IAEDK	75.7	49.1	27.5
TMPAE+DMPK	24.0	46.5	14.5
TMPAE+DDE	14.7	29.1	10.4

Table 6. Chemical resistance of cured epoxy samples in terms of % weight loss.

Aqueous solution (1M)	No. of days	Samples					
		PEMPAE+IAEDK weight loss [%]	PEMPAE+DMPK weight loss [%]	PEMPAE+DDE weight loss [%]	TMPAE + IAEDK weight loss [%]	TMPAE + DMPK weight loss [%]	TMPAE + DDE weight loss [%]
HCl	30	2.3	2.9	4.8	4.4	2.9	4.9
	60	3.8	4.3	6.6	3.9	5.1	7.2
	90	5.1	6.2	11.4	5.4	6.5	11.8
NaOH	30	2.9	3.1	4.6	3.5	3.8	4.9
	60	4.2	4.8	6.9	4.5	4.9	7.3
	90	5.7	6.6	12.2	6.3	7.1	12.8
NaCl	30	2.5	2.7	3.5	2.9	3.9	5.1
	60	3.9	4.5	6.8	4.1	5.3	7.6
	90	5.5	6.5	11.9	5.8	6.9	12.3

resins which is referred to the crosslinked polyester network formed by homopolymerization of epoxy functionality with anhydride groups.

3.6. Surface morphology analysis by SEM

Scanning electron microscopy (SEM) was used to analyze the destruction caused to the epoxy cured samples exposed to the chemical environment. The physical changes or surface morphology triggered by immersing the cured samples in different chemical solutions were observed by SEM images. The images in Figure 9a display the surface morphology of cured samples before immersion *i.e.* untreated with chemical solutions, whereas the images in Figure 9b show the surface changes that occurred after dipping in 1M HCl solution. The images clearly show

that the sample cured with imidoamine curing agent exhibited the least physical deterioration and were found to be most stable in a particular chemical environment. Besides this, the images for DDE cured samples show visible changes at the surface by the attack of the acidic solution. The signs of chemical corrosion can be seen as the cracks and roughening of the surface of cured resins which were smooth earlier [40]. These results ascertained that rosin epoxy cured with rosin imidoamine curing agent can be a substitute for coating application.

4. Conclusions

Rosin based two-component coating system; multi-functional epoxy resin (PEMPAE) and bifunctional imidoamine curing agent (IAEDK) were synthesized

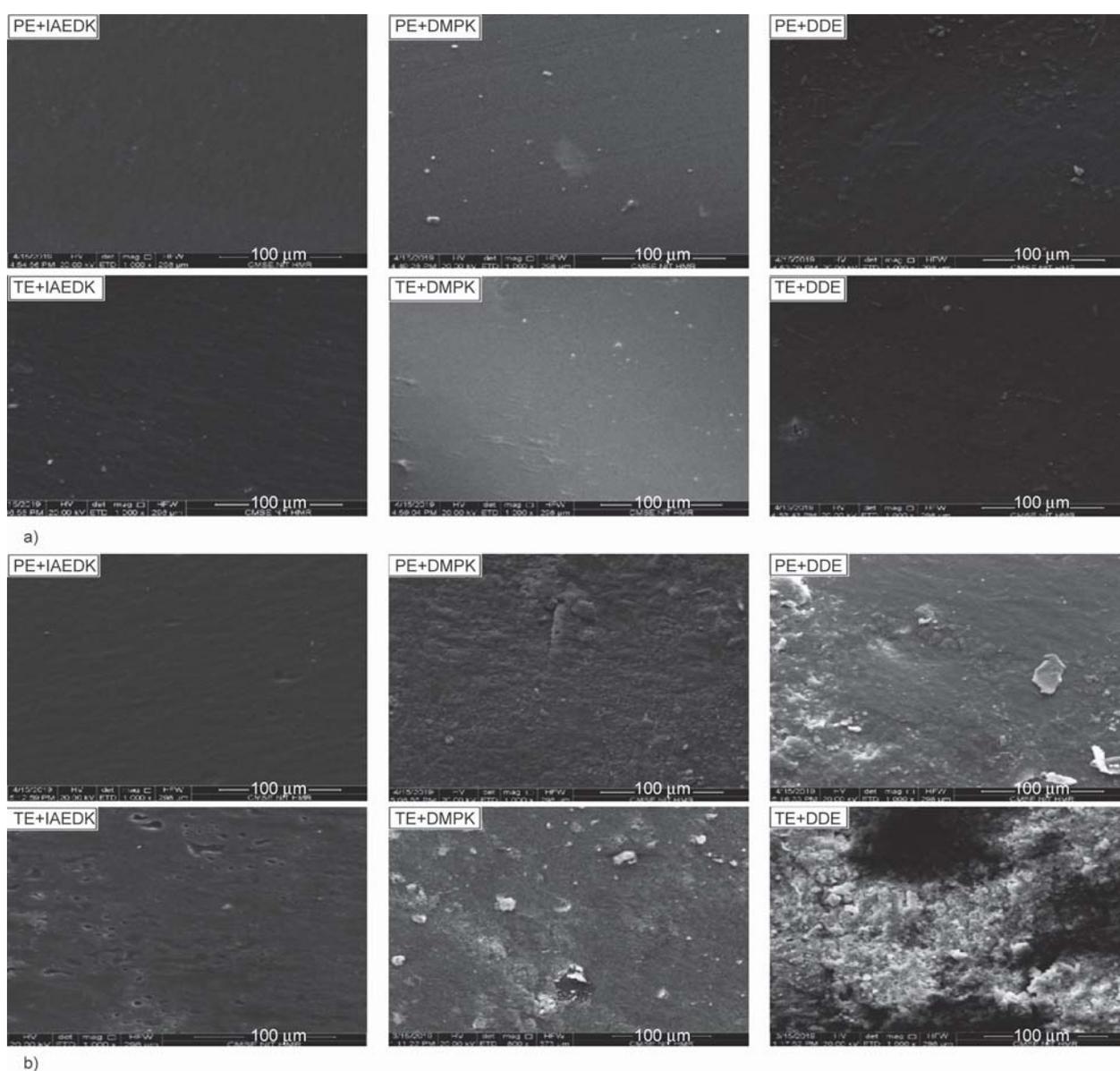


Figure 9. SEM images of cured epoxy resins (a) before immersion in chemical solutions and (b) after immersion in 1M HCl.

and their structural confirmation was done using FTIR, ¹H-NMR and ¹³C-NMR spectroscopic methods. Curing dynamics and thermal performance of rosin epoxy resin cured with imidoamine curing agent were studied and compared with epoxy system cured with synthesized anhydride type DMPK and commercial amine type DDE crosslinkers. The results revealed that imidoamine cured epoxy system exhibits low curing temperature i.e. high reactivity and high thermal performance than that of its synthetic precursors. Mechanical tests and chemical resistance were also performed and the bio-based cured system was found to be more resistant to the chemical environment and possessed better mechanical strength as imidoamine crosslinker imparts a high degree of crosslinking to the cured epoxy system. The surface morphology of cured samples exposed to chemicals also validates the chemical resistance analysis. Owing to the thermal, chemical and mechanical outcomes, fully bio-based epoxy systems are found to be a promising substitute to petrochemical coating materials that can address the environmental concerns too.

Acknowledgements

We would like to acknowledge Director, National Institute of Technology Hamirpur (H.P.) India for providing basic laboratory facilities and CMSE NIT Hamirpur for instrumental assistance. The authors are also grateful for financial support from the Department of Science and Technology, New Delhi, India (DST/SSTP/HP/481).

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