

Structure-Property Correlation Study of Bio-Based Multifunctional Vinyl Ester Resin in Presence of Methacrylated Lignin Model Compounds¹

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Abstract—Diels-Alder adduct of gum rosin and maleic anhydride (MPA) were treated with trimethylolpropane to obtain trimethylolpropane modified maleopimaric acid adduct (TMPA). This adduct was then epoxidized using epichlorohydrin and KOH as catalyst to synthesize an epoxy resin (TMPAE), which was further esterified using methacrylic acid in the presence of triphenyl phosphine as catalyst and hydroquinone as inhibitor to produce bio-based multifunctional vinyl ester resin (VTMPAE). This article also reports the synthesis of lignin model compounds i.e. methacrylated eugenol (ME) and methacrylated guaiacol (MG) as bio-based reactive monomers for vinyl ester resins. The chemical structures of all synthesized products were analyzed using FTIR, ¹H NMR and ¹³C NMR spectroscopic techniques. The thermal and mechanical properties of the samples were evaluated using Differential Scanning Calorimetry (DSC), Thermogravimetric Analyzer (TGA) and Universal Testing Machine (UTM), respectively. Chemical and corrosion resistance of the above cured VTMPAE samples coated on steel panels were also evaluated as a function of % weight loss by immersing the VTMPAE samples in 1 M HCl, 1 M NaOH, and 1 M NaCl solutions for 90 days. The morphological changes that appear upon such an exposure were also studied with the help of Scanning electron microscopy (SEM).

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INTRODUCTION

Dwindling petroleum resources have led to a growing urgency to develop novel polymers from renewable agricultural and forestry feed stocks. This can unhook the extensive dependence of synthetic polymers on fossil fuels and become a step towards sustainable development. The utilization of these renewable resources can consistently provide new raw materials as scaffolds for everyday products, which can effectively minimize the contribution to greenhouse effect and other environmental issues. Since vinyl ester resin is a versatile class of thermosetting polymers, they are extensively used in numerous industrial applications owing to their excellent handling characteristics, ease of cure, high strength, heat performance and corrosion resistance which include marine, industrial, building and construction etc. [1–7]. A quest to explore bio-based vinyl ester resin as one of the alternatives to petroleum based vinyl ester resin can serve to reduce the human footprints on the environment.

In the recent years, rosin components have attracted a renewed attention, notably as sources of monomers for polymer synthesis. Rosin acid extracted from the pine tree, is the oldest raw material for adhesive and coating industry either as such or as converted

derivatives. Gum rosin, which contains approximately 90% abietic acid and its isomers, is abundantly available as exudates of pines and conifers. It is a mixture of eight closely related rosin acids characterized by three fused six-carbon rings; double bonds that vary in number and location, and a single carboxylic acid group [8]. The ratio of these isomers in gum rosin depends upon the collection method and the species of the tree from which the gum rosin has been harvested. Moreover, due to the larger hydrogenated phenanthrene ring structure, rosin acids are similar in rigidity to petroleum-based cycloaliphatic or aromatic compounds and can be used as exceptional alternative to petroleum based vinyl ester resins [9]. The brittleness caused by phenanthrene ring of the gum rosin taken as the scaffold for the synthesis of novel MPA based vinyl ester resin can be overcome by the introduction of ether linkages in the polymer structure which in turn provides flexibility to the polymer.

The conventional vinyl ester resins are the addition product of epoxy resin and α - β unsaturated carboxylic acid. Since these resins possess very high viscosity, a reactive monomer is usually added to these in order to achieve workable viscosity levels during processing as in liquid molding techniques to fabricate large scale composite parts. Styrene is one such reactive monomer which is extensively used for this purpose. It also acts as

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a linear chain extender and improves the polymer performance since it delays the onset of gelation during curing and also addresses the diffusion limitation issue. However, since styrene has been designated as a hazardous pollutant due to high VOC, attempts are being made to replace it either by bimodal [10, 11] blends of VE monomers or by non-volatile fatty acid monomers obtained from renewable resources [12] in order to reduce emission. In this paper, we have also tried to include methacrylated lignin model compounds (LMC) as viable bio-based and less volatile candidates to completely replace styrene as reactive monomer.

Intensive research efforts have also been devoted to develop new series of multifunctional vinyl ester resins by chemical and physical modifications of the classical linear shaped vinyl ester resins in previous few years. The approach to introduce multifunctionality in vinyl ester resin is not only to provide just a certain amount of protection towards chemical environment but also to provide additional functions e.g. improved adhesion, low abrasion and high strength.

In the present article, we have used gum rosin as a scaffold material to synthesize multifunctional bio-based vinyl ester resin and further investigated the thermal, mechanical properties and chemical resistance of the synthesized resin using bio-based and non-volatile methacrylated lignin model compounds (LMCs) as reactive monomers.

EXPERIMENTAL

Materials

Gum rosin (WW grade), maleic anhydride (Lobachemie, 99% pure), *p*-toluenesulfonic acid (pTSA) (Lobachemie, 99% pure), and trimethylolpropane (Lobachemie, 98% pure) were used for the synthesis of maleopimaric acid (MPA) adducts and esterification of adduct with trimethylolpropane. Epichlorohydrin L.R. grade (Lobachemie, 99% pure), Potassium hydroxide pellets (Merck, $\geq 85\%$ pure) were used for preparation of epoxy resin. Methacrylic acid (Lobachemie, 99% pure) and triphenylphosphine (Lobachemie, 98% pure) were used for synthesis of vinyl ester resin based on maleopimaric acid (MPA). Eugenol (Lobachemie, 99% pure), (Lobachemie, 99% pure), Methacrylic anhydride (Lobachemie, 94% pure), and 4-dimethylaminopyridine (DMAP) (Lobachemie, 99% pure), were used for the synthesis of methacrylated eugenol (ME) and methacrylated guaiacol (MG). Styrene (ACROS ORGANICS, 99.5% pure), methacrylated guaiacol (MG) and methacrylated eugenol (ME) were used as reactive monomers in the present study.

Procedures

Synthesis of MPA (maleopimaric acid adduct). Gum rosin (10 g) was heated to 180°C in 100 mL round bottom flask equipped with mechanical stirrer and a Liebig condenser. The temperature was main-

tained for 3 h to complete the isomerization of abietic structure to levopimaric structure under N_2 atmosphere. The reaction mixture was then cooled to 120°C and 30 mL acetic acid, 2.35 g of maleic anhydride and 0.46 g of *p*-toluene sulphonic acid (pTSA) was added. The reaction mixture was allowed to reflux for 12 h. A yellow solid crude product obtained upon cooling was recrystallized from acetic acid to obtain white crystals of pure MPA (yield: 91%).

Synthesis of TMPA (esterification of MPA with trimethylolpropane). A mixture of trimethylolpropane (3 moles), MPA (1 mole), pTSA (1 wt %) based on the total weight of reactants and 20 mL of xylene were placed in round bottom flask fitted with mechanical stirrer and Dean and Stark apparatus. The mixture was allowed to reflux until 3 moles of water was collected. A dark yellow solid product was obtained (yield: 93%). The product was then washed with hot water to remove unreacted trimethylolpropane. Xylene was distilled off from the reaction product under reduced pressure. The percentage of hydroxyl functionalities in TMPA were confirmed by using conventional acetic anhydride/pyridine method [13]. Practically the percentage of hydroxyl groups in TMPA was found to be 12% which is close to theoretical value of 12.5%. This confirmed the esterification of MPA with trimethylolpropane.

Synthesis of epoxy resin based on TMPA (TMPAE). 30 g of TMPA and 220 mL of DMSO were mixed for 15 minutes at 24°C into a reaction vessel equipped with a mechanical stirrer and Liebig condenser. Then finely grounded KOH (2 equivalents per hydroxyl group in TMPA) was added at once, and the mixture stirred for another 15 min at 24°C . The reaction mixture was stirred vigorously with a mechanical stirrer and cooled to $15\text{--}20^\circ\text{C}$ with an ice bath. Epichlorohydrin (5 equivalents per hydroxyl group in TMPA) was added dropwise over 1.5 h. After completing the addition, the reaction mixture was maintained at 24°C and further stirred for 16 h. The reaction product was extracted with equal amounts of water and dichloromethane mixture. The volatile fractions of dichloromethane were distilled off under reduce pressure from light yellow colored epoxy resin (yield: 85%). The epoxide equivalent weight (EEW) of the TMPAE epoxy resin was determined as 199.68 g/eq by pyridinium chloride method [14].

Synthesis of vinyl ester resin based on TMPAE (VTMPAE). Vinyl ester resin was prepared using 1 : 0.9 molar ratios of trimethylolpropane modified MPA based epoxy resin and methacrylic acid in the presence of triphenyl phosphine (1 phr by weight of epoxy resin) and hydroquinone (200 ppm) at $85 \pm 1^\circ\text{C}$ for three and a half hours to obtain a product (yield: 95%) with acid value of ~ 7 mg of KOH/g solids determined according to ASTM D 1636.

Synthesis of bio-based methacrylated guaiacol (MG) and methacrylated eugenol (ME) as reactive monomers. A mixture of 4-dimethylaminopyridine (DMAP, 2 mol % of methacrylic anhydride) and

eugenol/guaiacol was charged to 100 mL round bottom flask and contents were stirred on a magnetic stirrer. N₂ gas was subsequently purged for 1 h to the reaction vessel to remove moisture and oxygen, then, methacrylic anhydride (1.2 mol) was added. For the first three hours, the reaction mixture was stirred at room temperature. After three hours, the temperature was increased to 45°C for 24 h. The reaction mixture was cooled to room temperature and diluted with 150 mL ethyl acetate. Unreacted methacrylic acid and methacrylic anhydride was removed by washing organic phase with saturated aqueous NaHCO₃ solution until carbon dioxide no longer evolved. The organic phase was then washed with 1.0 M aqueous NaOH solution succeeded by 1.0 M aqueous HCl solution. The pale yellow colored liquid (yield 98%) was then dried over sodium sulphate and finally ethyl acetate was removed by distillation under reduced pressure [15].

Characterization

Structural characterization. The structural characterization of MPA, TMPA, TMPAE, VTMPAE, methacrylated guaiacol (MG) and methacrylated eugenol (ME) was done using FTIR, ¹H NMR and ¹³C 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 ¹H NMR and ¹³C NMR spectra of these samples were recorded using Bruker Avance II 400 NMR spectrometer, CDCl₃ as solvent and tetramethylsilane as an internal standard.

Determination of physical properties. The refractive indices (RIs) of the VTMPAE samples containing styrene, MG and ME were measured by means of an Abbe's refractometer. Viscosities of the VTMPAE/VPMPAE samples containing 40% wt/wt styrene, MG and ME were measured by using Brookfield viscometer (LV DV II + Pro, Brookfield, USA) using spindle no. L62 at 120 rpm. Density measurements for the above samples were performed at 20°C using Pycnometer.

Gel Permeation Chromatography (GPC)

Molecular weight of *o*-cresol epoxy novolac based vinyl ester resin (VEOCN) was recorded with Turbo matrix—40 (Perkin Elmer) Gel Permeation Chromatograph. The column used for GPC calibration was of crosslinked polystyrene. Tetrahydrofuran (THF) was used both as mobile and stationary phase for the experiment.

Evaluation of Cured VTMPAE Resin Samples as High Performance Coatings

Curing and decomposition behavior of MPA based vinyl ester resin (VTMPAE). The samples for curing and decomposition behavior were prepared by mixing

10/4/0.2 (wt/wt) of trimethylolpropane modified MPA based vinyl ester resin (VTMPAE), styrene/methacrylated guaiacol (MG)/methacrylated eugenol (ME) as reactive monomers and free radical initiator-benzoyl peroxide, respectively, in small glass vial and stirred vigorously with a glass rod at 30°C until the mixtures became homogeneous in nature. A Diamond DSC (Perkin Elmer) was used to record the DSC scans of the above samples by taking ≈2 mg of the sample into shallow aluminium cover under dynamic conditions with program rate of 10 deg/min from 35°C to the temperature at which the exothermic reactions were completed.

From the dynamic DSC scans, a temperature was selected at which an appreciable rate of curing could be observed. DSC runs under isothermal conditions at the selected temperatures were then carried out to determine the apparent time required for the completion of each of the curing reactions. The curing conditions (temperature and time) thus determined were used to cure the resin samples for subsequent studies on thermal stability. An EXSTAR TG/DTG 6300 was used to record TG/DTG/DTA traces in nitrogen atmosphere (flow rate = 200 mL/min) at heating rate of 10 deg/min with sample size 11 ± 5 mg. The relative thermal stability of the resin was quantitatively estimated by comparing the temperatures for a particular degree of weight loss.

Mechanical behavior. The mechanical properties such as compressive strength (as per ASTM D3410), flexural strength (as per ASTM D790) and tensile strength (as per ASTM D3039) of trimethylolpropane modified MPA based vinyl ester resin samples cured using styrene, methacrylated guaiacol (MG) and methacrylated eugenol (ME) as reactive monomers were determined by Hounsefield-25KN universal testing machines at deformation rate of 2 mm/min. The samples for the analysis of mechanical performance were prepared by mixing 10/4/0.2 (wt/wt) of trimethylolpropane modified MPA based vinyl ester resin (VTMPAE), styrene/methacrylated guaiacol (MG)/methacrylated eugenol (ME) as reactive monomers and free radical initiator-benzoyl peroxide, respectively, in a beaker. The mixture (VTMPAE+Styrene/MG/ME+benzoyl peroxide) was then poured into the specially designed molds of dimension (150 × 150 × 5.0) mm³ and cured at 90 ± 5°C under load of 100 kg/cm² for 12 h in a compression molding machine. The samples were cut with the help of metallurgical saw into different sizes required for the type of the test to be carried out according to the test specifications.

Chemical resistance and corrosion resistance of cured VTMPAE resin samples. Mild steel panels (15 cm × 10 cm), prepared according to British standard specification 1449, were used to evaluate the chemical and corrosion resistance of VTMPAE samples containing styrene, MG and ME as reactive monomers. One side of the panel was coated using hand layup method with coal tar epoxy primer to protect against chemical environment used to evaluate the chemical and corrosion resistance. While the tested side of the panel was coated with VTPMAE resin containing sty-

rene, MG and ME as reactive monomers and cured at $90 \pm 5^\circ\text{C}$ for 24 h. Chemical and corrosion resistance behavior in terms of percent weight loss of the cured resin samples coated on mild steel panels was studied by plunging the coated panels of identified weights in 1 M HCl, 1 M NaOH, and 1 M NaCl solutions for 90 days at room temperature. Percent weight loss was then calculated using the following formula

$$\% \text{ weight loss} = \frac{W_i - W_f}{W_i} \times 100,$$

where W_i —dry weight of the sample before immersion, W_f —dry weight of the sample after immersion.

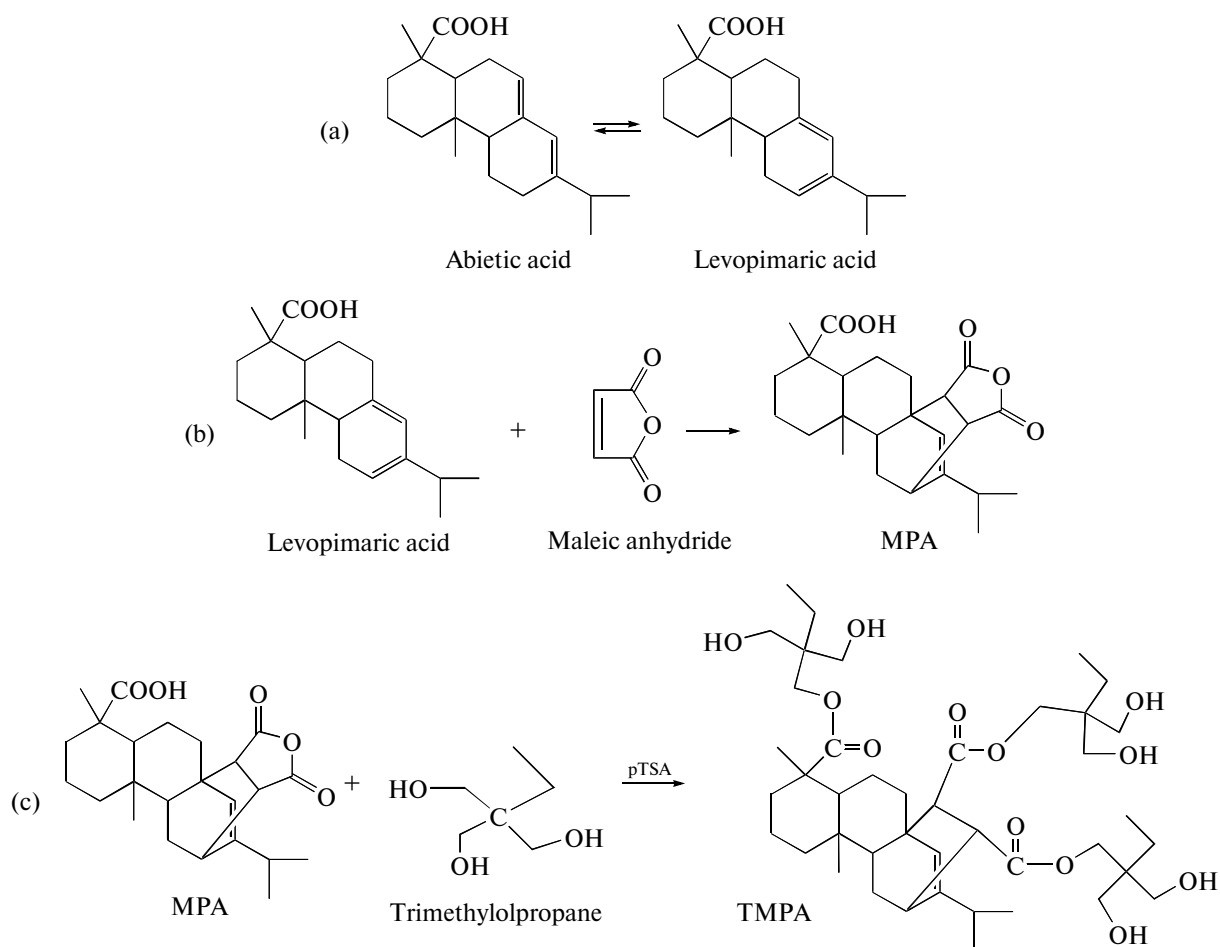
Scanning electron microscopy (SEM). SEM was also used to analyze morphological changes on the surface of coated VTMPAE resin samples (containing styrene, MG and ME as reactive monomers) due to chemical exposure given to study the chemical and corrosion resistance of the cured VTMPAE resin samples. The SEM analysis was performed by JSM-6610 machine and to enhance the conductivity of the sam-

ples thin film of gold was mounted on the samples before the SEM photographs were taken.

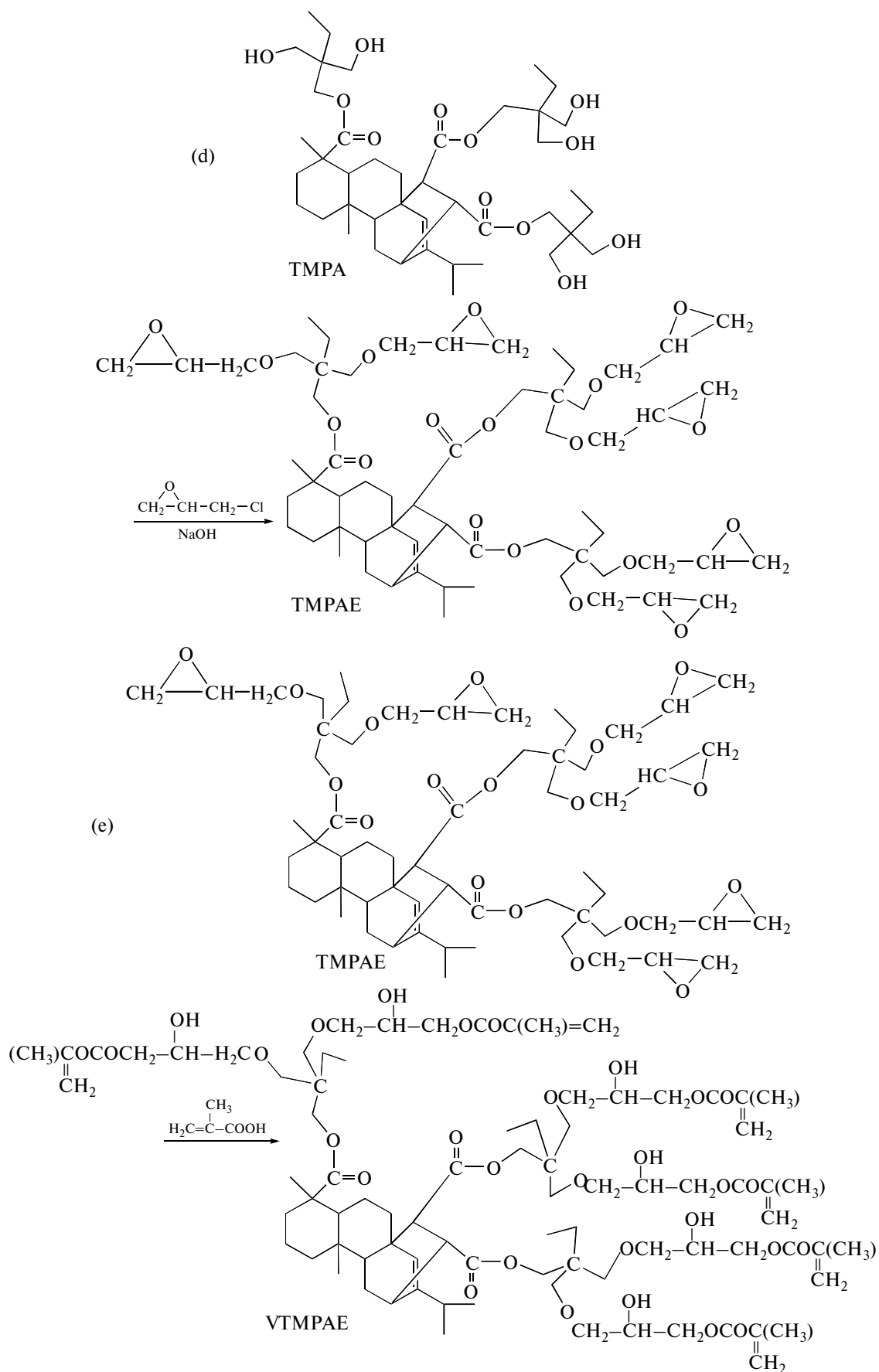
RESULTS AND DISCUSSION

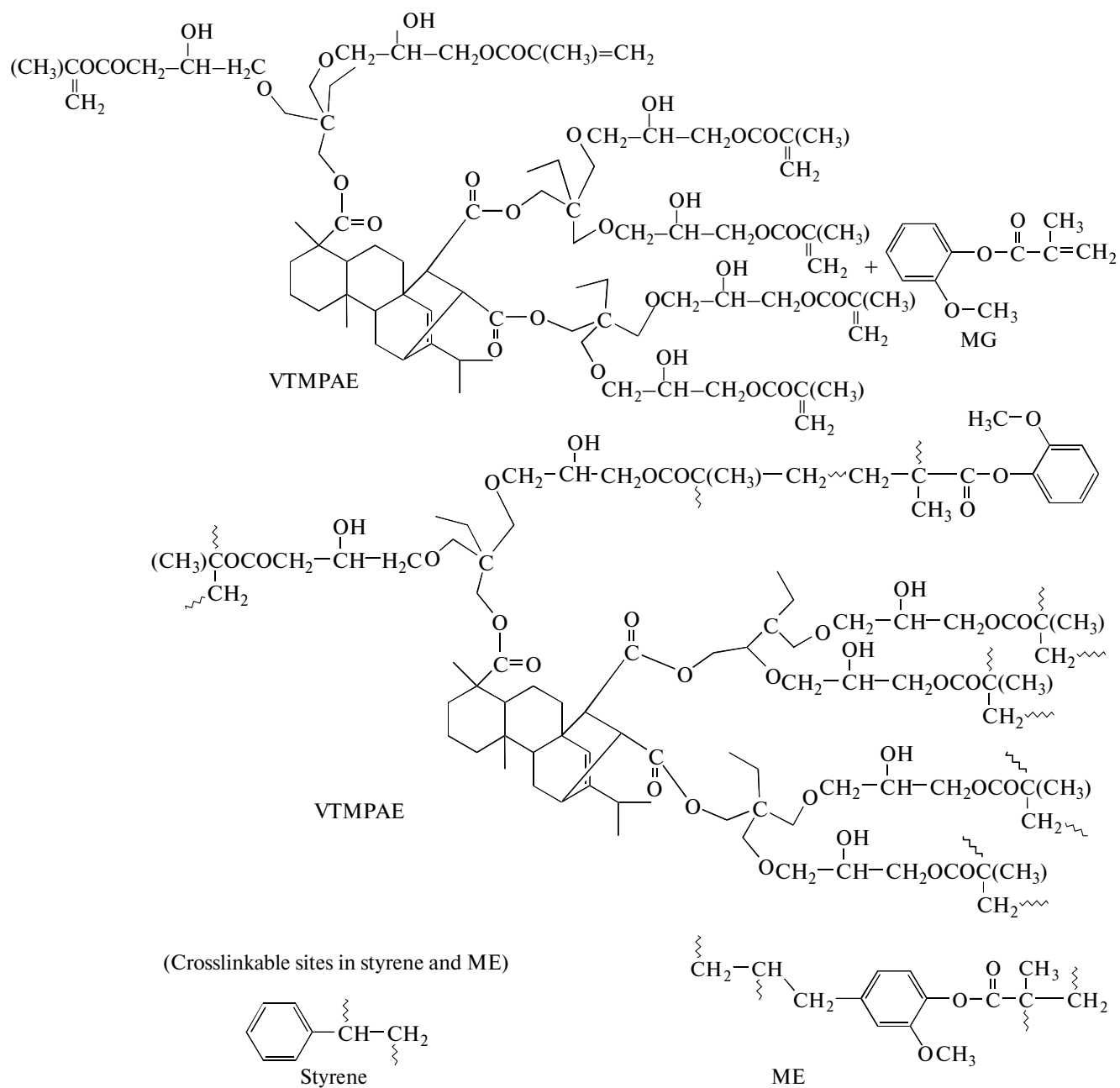
Synthesis of MPA, TMPA, TMAPAE, and VTMPAE

Gum rosin is a mixture of isomeric rosin acids out of which only levopimaric acid can undergo Diels-Alder cycloaddition reaction. However, the other isomers can get isomerized into levopimaric acid at elevated temperatures without the use of any solvent or catalyst. Scheme 1 shows the complete reaction procedure for the synthesis of vinyl ester resin (VTMPAE) from gum rosin and Scheme 2 depicts the curing of VTMPAE with MG as reactive monomer and benzoyl peroxide (BP) as free radical initiator. The synthetic route of MPA, where isomerization of abietic acid to levopimaric acid is carried out at 180°C for three hours, has been shown in Scheme 1a. The levopimaric acid is, then treated with maleic anhydride for next three hours to obtain MPA adduct as shown in Scheme 1b.



Scheme 1.





Scheme 2.

The structure of this adduct can be confirmed by FTIR as well as ^1H NMR spectroscopy. Figure 1 shows the FTIR spectrum of MPA. A broad absorption peak ranging from $3000\text{--}3300\text{ cm}^{-1}$ due to carboxylic $-\text{OH}$ stretching present in MPA can be observed in the spectrum. Two stretching bands in the carbonyl region at 1843 and 1779 cm^{-1} display the presence of anhydride group which confirm the Diels-Alder reaction between gum rosin and maleic anhydride and lead to the formation of MPA. The Diels-Alder reaction between gum rosin and maleic anhydride is further supported by the ^1H NMR spectrum (Fig. 2). In ^1H NMR spectrum of abietic acid shown

in Fig. 2a, the signals at $0.8\text{--}2.3$ ppm are attributed to the protons on the three fused six-carbon rings and the peaks at 5.36 and 5.77 ppm are due to the protons on the unsaturated carbon whereas the appearance of only one resonance signal at 5.3 ppm in Fig. 2b due to the proton of unsaturated carbon after the Diels-Alder cycloaddition reactions confirm the adduct (MPA) formation. Other peaks at $3.00\text{--}3.15$ ppm (proton 2), $2.7\text{--}2.8$ ppm (proton 3), $2.40\text{--}2.55$ ppm (proton 4), $2.2\text{--}2.4$ ppm (proton 5) have also been identified. The MPA adduct is further reacted with trimethylolpropane in order to improve the flexibility of the synthesized resin (Scheme 1c) and to introduce more num-

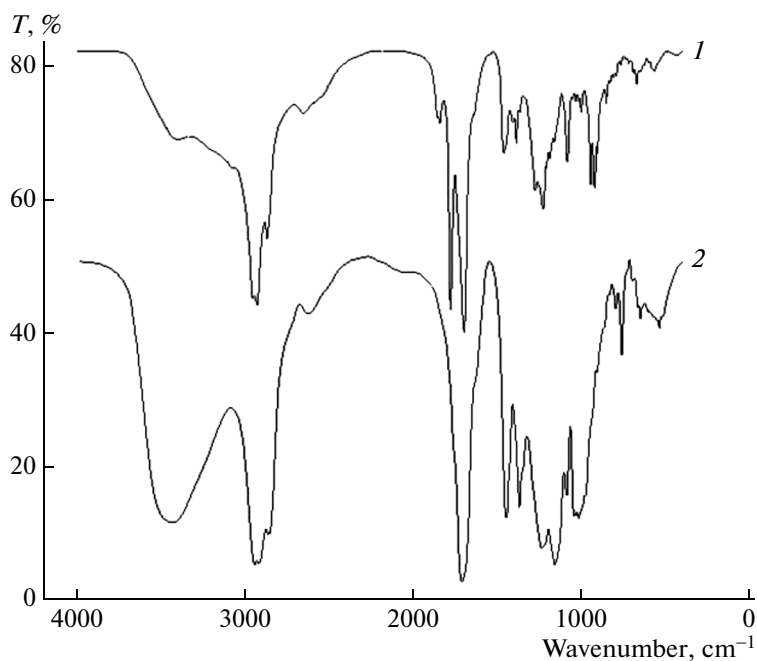


Fig. 1. The FTIR spectra of (1) MPA and (2) TMPA.

bers of hydroxyl groups in the resin which further are epoxidized and the epoxy groups subsequently are esterified with methacrylic acid in order to yield vinyl ester resin having improved thermal stability, chemical resistance and mechanical properties. The ^1H NMR spectrum of TMPA in Fig. 2c shows a characteristic peak of hydroxyl protons at 3.7–4.3 ppm which proves the esterification of MPA adduct with trimethylolpropane. Retention of the peak at 5.36 ppm also proves the fact that the adduct (MPA) structure is intact when esterification reaction is carried out. FTIR spectrum in Fig. 1 also shows the disappearance of the anhydride peaks and appearance of peaks due to carbonyl group at 1730 and 1700 cm^{-1} which again confirm the esterification reaction.

The formation of tetraglycidyl ether (Scheme 1d) of rosin acids is carried out by reacting TMPA with epichlorohydrin (ECH) in the presence of KOH as catalyst at $15 \pm 1^\circ\text{C}$. The epoxide functionality introduced during the epoxidation of TMPA is confirmed by epoxide equivalent weight determination. The epoxide equivalent weight of the epoxy resin is calculated to be 199.68 g/eq. which is nearly equal to the theoretical EEW i.e. 183.9 g/eq. and is approximately the one sixth of the theoretical average weight of the TMPAE which is 1103.4 g/mol, which means the epoxide functionality in TMPAE epoxy resin is found to be 5.5 which confirms the epoxidation of all the six hydroxyl groups present in TMPA. The chemical structure of epoxy resin is characterized by FTIR (Fig. 3) which shows the characteristic band due to symmetrical stretching or ring breathing frequency of epoxy ring at 1253 cm^{-1} and asymmetrical C–O–C

stretching in aryl alkyl ethers at 1174 cm^{-1} . The ^1H NMR spectrum (Fig. 4a) of the resin confirms epoxidation of the hydroxyl group since the signal due to hydroxyl protons at 4 ppm cannot be observed. The signals due to methylene protons (proton 5) and methine proton (proton 4) of the oxirane ring appear at 2.6 and 2.8 ppm, respectively.

Trimethylolpropane modified MPA based vinyl ester resin VTMPAE sample (Scheme 1e) is prepared using trimethylolpropane modified MPA based epoxy resin (TMPAE) with methacrylic acid 1 : 0.9 molar ratio in the presence of triphenyl phosphine with acid value ~ 7 mg KOH/g solid and is further used to study the thermal and mechanical properties using styrene (Sty), methacrylated guaiacol (MG) and methacrylated eugenol (ME) as reactive monomers. The synthesis of the VER is usually catalyzed by tertiary amines, phosphines, and alkalies or –onium salts [16–21] in the temperature range of 80–110 $^\circ\text{C}$ and taking reactants in stoichiometric ratio. It has been observed that complete esterification of the epoxy resin in practice is difficult because of the gelation of the product before acid value below 10 is attained. Therefore, an excess of epoxide resin is always employed in the esterification reactions [22]. Figure 5 illustrates the change in the acid value with reaction time. It is apparent from the figure that the acid value decreases with the reaction time. The results are typical of the behavior generally observed in catalyzed polyesterification reactions. It is apparent from the plot that the decrease in acid value in the initial stages of the reaction is not linear, which is due to the high

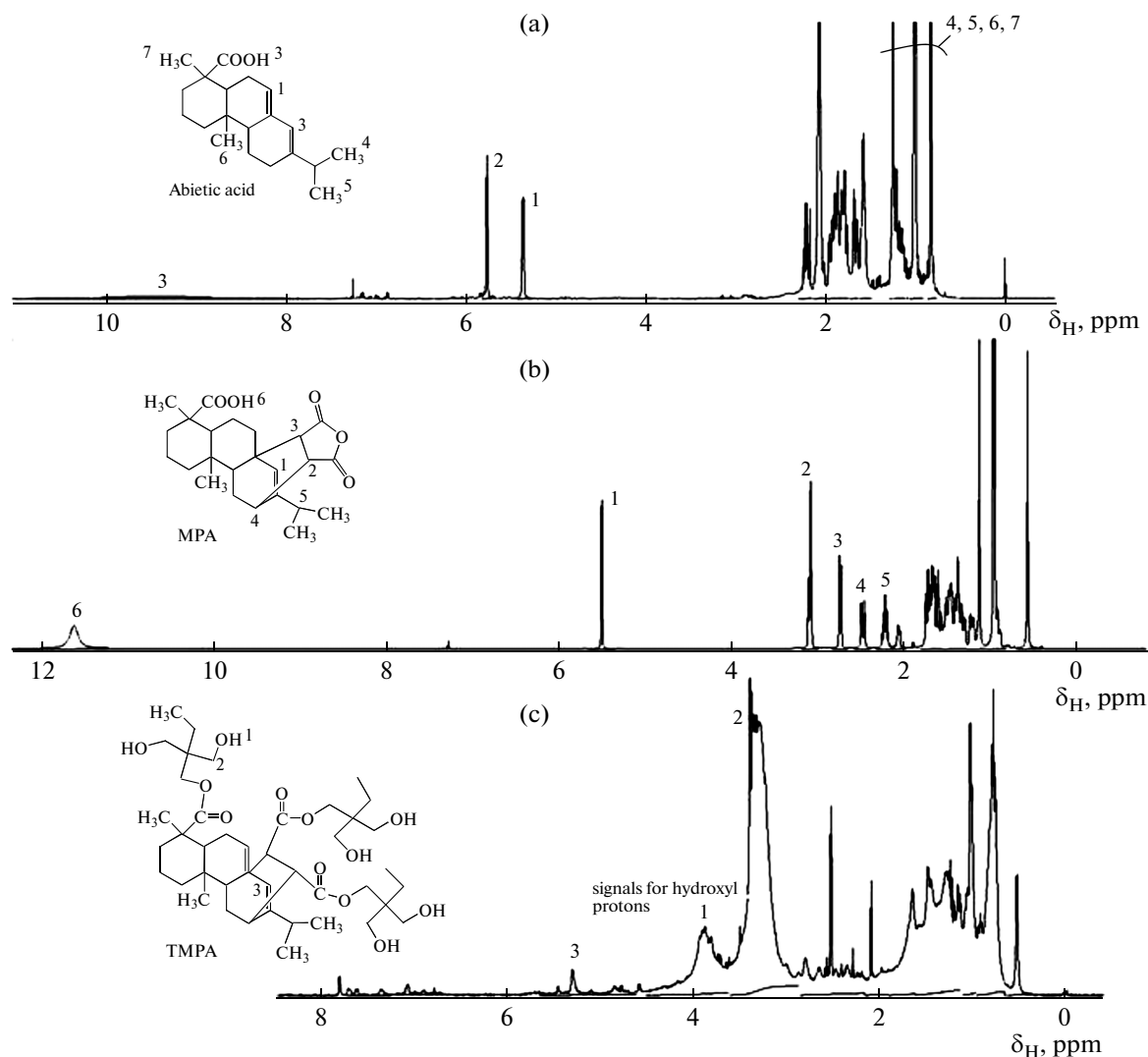


Fig. 2. The ^1H NMR spectra of (a) abietic acid, (b) MPA and (c) TMPA.

concentration of the reactive sites and greater possibility of association of acidic group with epoxide groups.

The typical GPC graph for the VTMPAE has also been shown in Fig. 6. A single peak has been observed in the GPC graph, which confirms the absence of side reactions during the synthesis of vinyl ester resin (VTMPAE). FTIR spectrum of VTMPAE in Fig. 3, shows the appearance of distinguished broad absorption band due to secondary hydroxyl group at 3433 cm^{-1} , peaks at 1715 and 1170 cm^{-1} due to carbonyl groups of methacrylate and peak at 1631 cm^{-1} due to $\text{C}=\text{C}$ stretching of methacrylate groups verifies the formation of VTMPAE. The methacrylated epoxy group shows distinct signals in ^1H NMR spectrum of VTMPAE (Fig. 4b), where the methylene protons of methacrylate group appear at 6.15 and 5.55 ppm (protons 2), whereas the signal at 2.1 ppm is due to methyl protons of methacrylate end group. Since, it is practi-

cally difficult to esterify all the epoxy groups present in TMPAE as a result of which proton resonance signals at 2.6, 2.9, and 3.3–3.4 ppm due to $-\text{CH}_2-$, $-\text{CH}$, and $\text{O}-\text{CH}_2$ protons of residual epoxy ring are also observed. Figure 7 shows the ^{13}C NMR spectrum of VTMPAE in which resonance signals for $-\text{CH}_3$ (carbon 7) and $=\text{CH}_2$ (carbon 1) of methacrylate group appear at 18.2 and 125.1 ppm, respectively. The resonance signals at 167.42, 173 and 178 ppm region are due to $-\text{O}=\text{C}-$ of ester groups at carbon 4, 2, and 3 respectively present in vinyl ester resin (VTMPAE). The resonance signals for $-\text{C}-$ (carbon 5) and $=\text{CH}$ (carbon 3) present in the gum rosin moiety appear at 135 ppm and 129.5 ppm, respectively. The resonance signals in the region 15–54 ppm are observed due to the $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ carbons present in gum rosin, whereas resonance signals from 65–77 ppm are observed due to the $-\text{O}-\text{CH}_2-$ carbons present in the

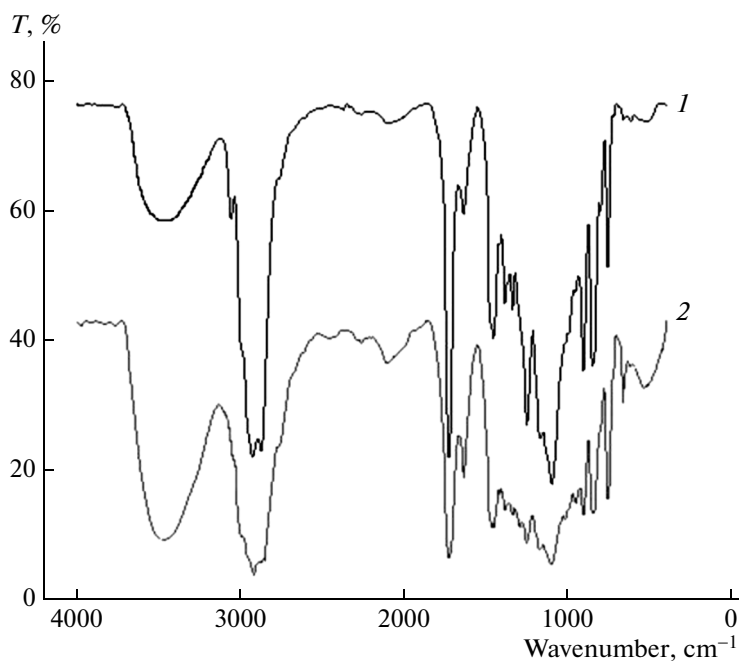


Fig. 3. The FTIR spectra of (1) TmpAE and (2) VTmpAE.

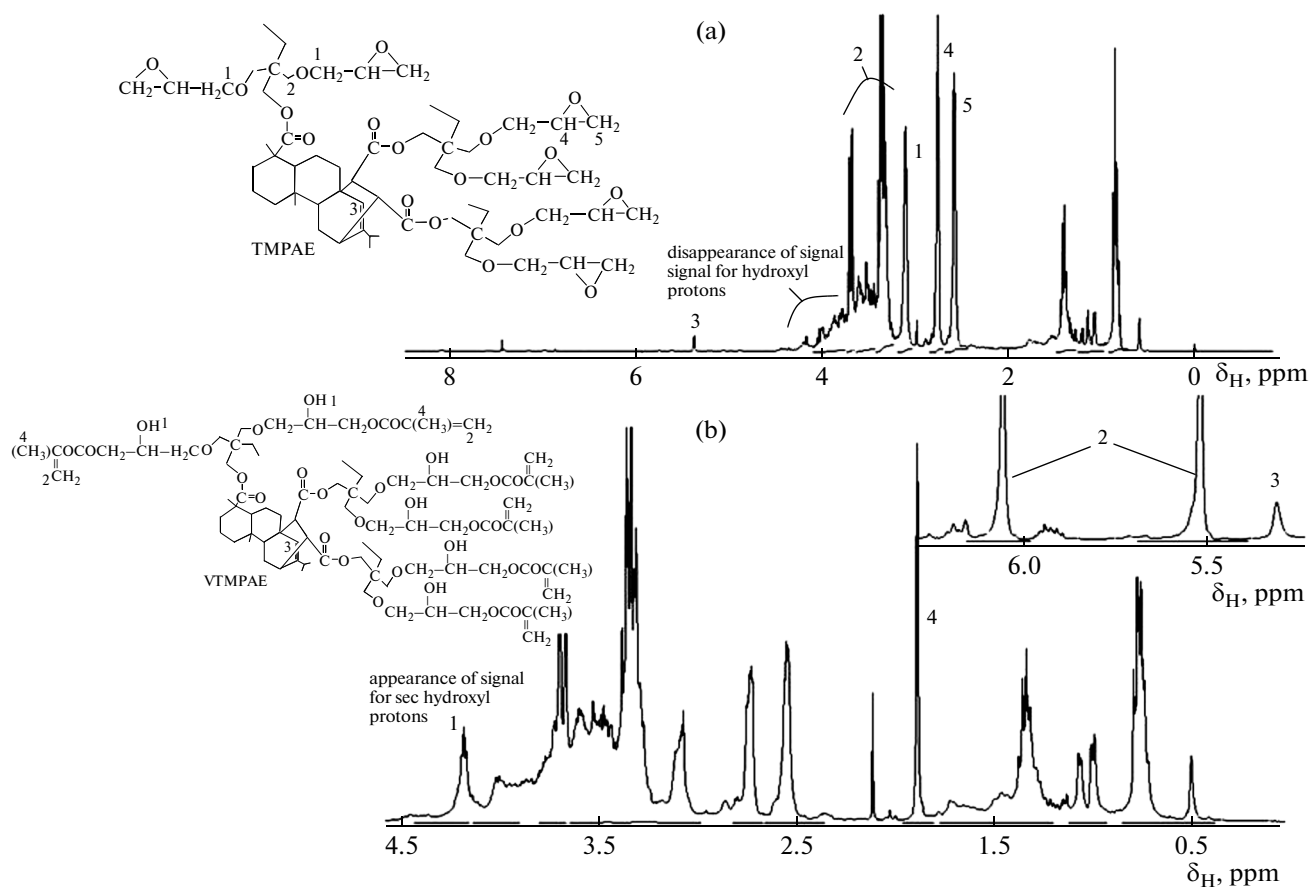


Fig. 4. The ¹H NMR spectra of (a) TmpAE and (b) VTmpAE.

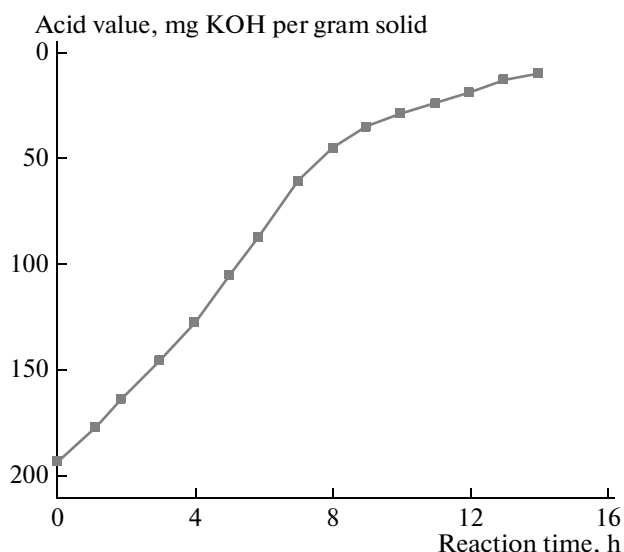


Fig. 5. Acid value versus reaction time graph for VTMPAE.

VTMPAE. The weight average molecular weights (\overline{M}_w) and physico-chemical properties of all the synthesized products are summarized in Tables 1 and 2.

Spectroscopic Analysis of Bio-Based Reactive Diluents

FTIR spectra shown in Fig. 8a illustrates the notable absorption peaks due to carbonyl wagging vibration at 1739 cm^{-1} , terminal C=C wagging vibration at $1638\text{--}1637\text{ cm}^{-1}$ and terminal C=CH₂ bending vibration at $947\text{--}946\text{ cm}^{-1}$ due to methacrylate group in methacrylated eugenol (ME), respectively. Moreover,

C=CH₂ bending vibration associated with allyl group present in methacrylated eugenol (ME) is also observed at 916 cm^{-1} . In the ¹H NMR spectrum in Fig. 8b of methacrylated eugenol (ME), characteristic resonance signals due to aromatic protons at 6.8–7.1 ppm, =CH₂ protons of methacrylate group at 5.9 and 6.3 ppm, –O–CH₃ protons at 3.7 ppm, and –CH₃ protons of methacrylate group at 1.9 ppm are observed with additional proton resonance signals for allyl group at 3.3, 5.1, and 5.8 ppm due to –CH₂, =CH₂, and –CH protons, respectively. A similar ¹H NMR spectrum is also observed for MG with the only difference in the absence of signals of allylic protons.

Evaluation of Curing Behavior of VTMPAE Samples

The curing behavior of vinyl ester resins varied with the number of functional end groups i.e. multifunctionality present in vinyl ester resin and different reactive monomers. The typical DSC scans for the curing of the samples prepared by mixing 10/4/0.2 (wt/wt [23]) of VTMPAE with styrene, methacrylated guaiacol (MG) and methacrylated eugenol (ME) (40% wt/wt), respectively, at a program rate of 10 deg/min have been depicted in Fig. 9. It can be observed from the figure that the heat flow for the curing of VTMPAE with all the monomers displays a single exothermic peak and these exothermic transitions are in the range of 85–150°C. Usually, under the same curing conditions, the onset temperature (T_i) and peak temperature (T_p) can be taken as an indicator of reactivity of the reactive monomers with vinyl ester resin during curing reactions. The T_i and T_p of the vinyl ester resins also show dependence on the multifunctional end

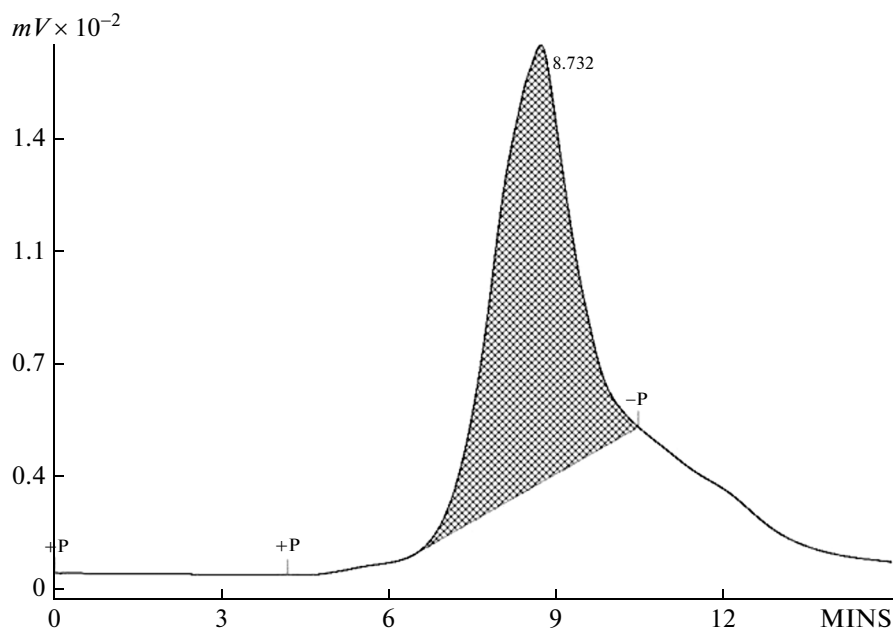


Fig. 6. Typical GPC graph for VTMPAE.

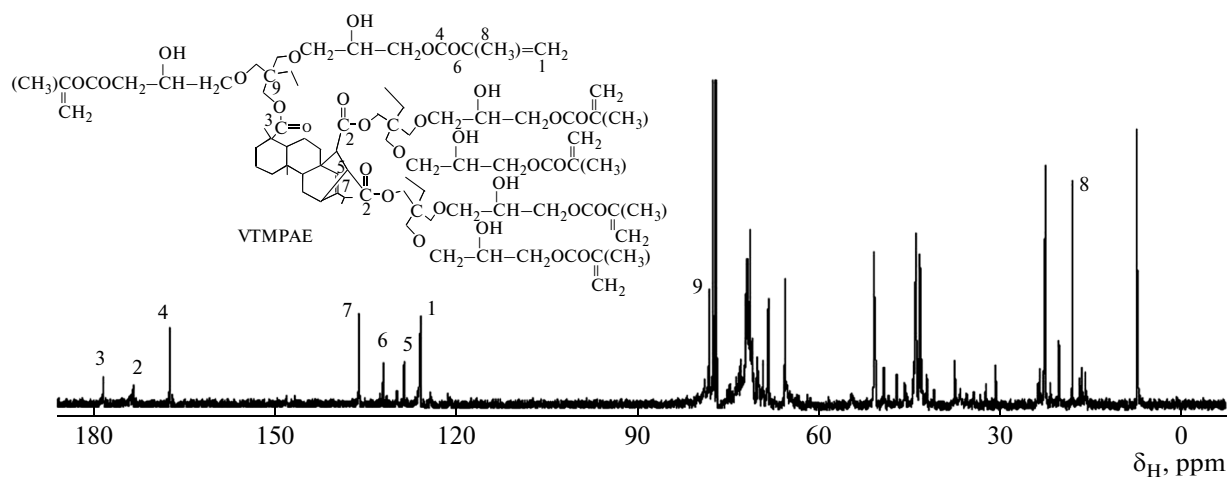


Fig. 7. The ^{13}C NMR of VTMPAE.

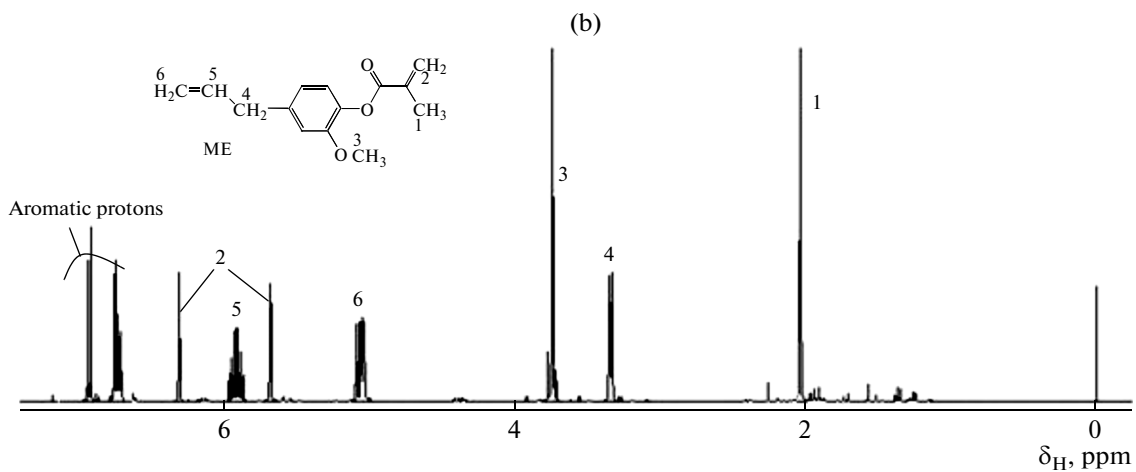
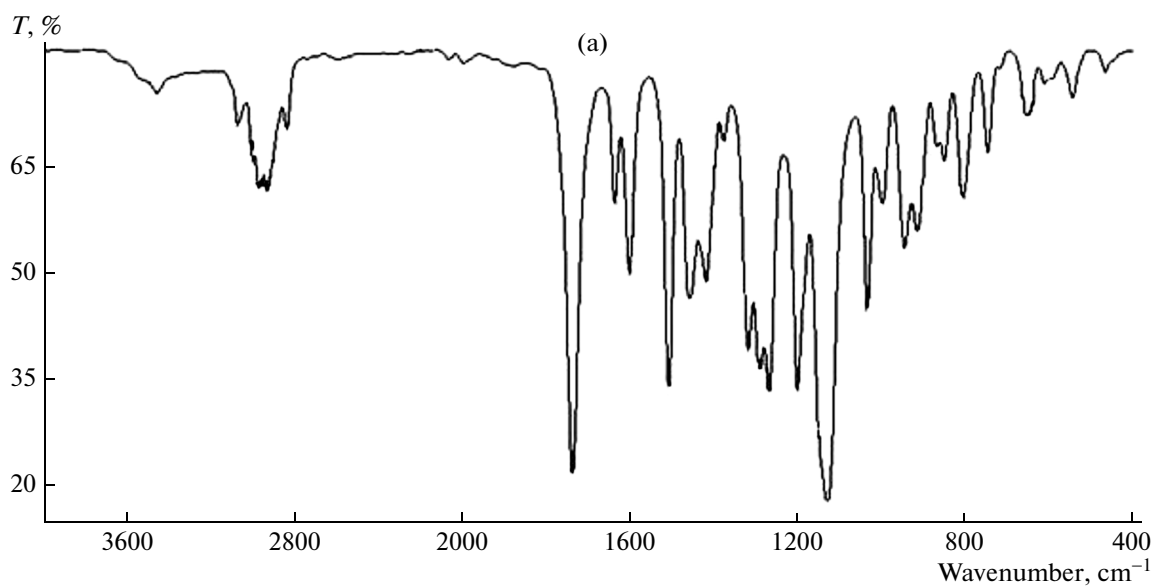


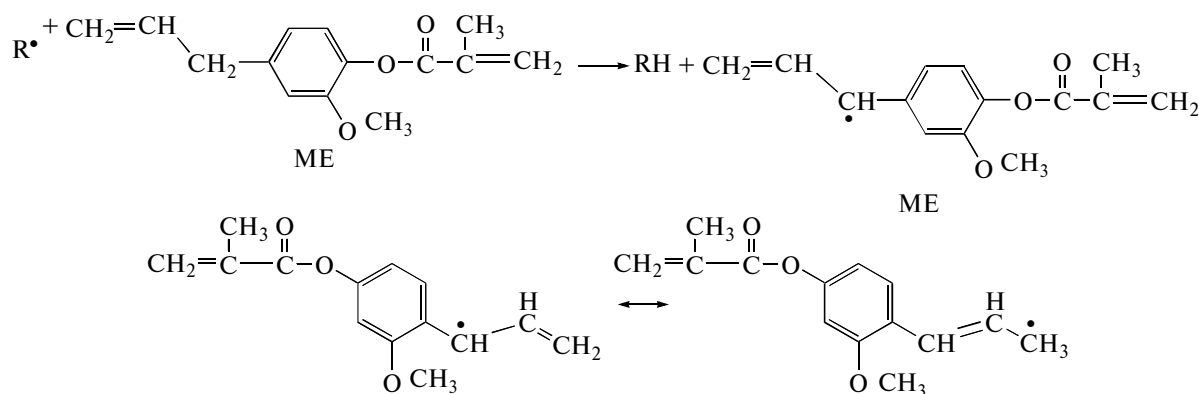
Fig. 8. (a) FTIR and (b) ^1H NMR of methacrylated eugenol (ME).

Table 1. Molecular weights of all the synthesized products determined by GPC

Samples	Weight average molecular weight, (\overline{M}_w), g/mol	
	theoretical values	experimental values
MPA	400.512	398.67
TMPA	767.003	775.4
TMPAE	1103.385	1120
VTMPAE	1619.921	1640.5

groups in high molecular weight macromolecules. Lower T_i and T_p values are related to formation of strong dipolar interactions between the functional end groups present in the multifunctional vinyl ester resins and polar moieties present in different reactive monomers taken for the study. The onset temperatures (T_i) are 97.77, 91.9, and 94.5°C and peak temperature (T_p) are 119.4, 105.5, and 110.27°C for VTMPAE samples containing styrene, MG and ME, respectively. It can also be observed that the onset and peak temperatures for VTMPAE samples containing MG and ME are lower than that of sample containing styrene which

signifies that MG and ME are more reactive to VTMPAE 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. Furthermore, methacrylate radicals present in MG and ME are more polar as compared to styrene and consequently more reactive towards the vinylic C=C of methacrylate group present in the VTMPAE. On comparing the reactivity of ME and MG from Fig. 9, it can be seen that methacrylated eugenol is found to be less reactive than MG, since the allyl substituent present at para position to methacrylate group in ME form a stable free radical due to resonance stabilization and this stable free radical of allyl substituent present in ME competes with the normal propagation reaction step during the curing reaction between ME and VTMPAE resin system which inevitably disrupts and decelerate chain growth by degradative chain transfer (DCT) reaction [24]. The resulting allyl free radical does not readily add to the vinyl ester monomer but once all the methacrylic C=C groups of the ME are consumed in copolymerization, the allylic C=C groups start copolymerizing [25]. Resonance stabilization of allylic free radical in the case of methacrylated eugenol has been shown in Scheme 3.

**Scheme 3.** Resonance stabilization of an allylic free-radical in ME molecule.

Evaluation of Thermal Stability of VTMPAE Samples

The thermal decomposition of thermosetting polymers is commonly determined by thermogravimetric (TGA) analysis under nitrogen atmosphere. TG curve

reveals the weight loss of substances in relation to the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of weight loss. The thermal stability of thermo-

Table 2. The physico-chemical properties of all reactive monomers and VTMPAE resin samples containing these reactive monomers

Properties	MG	Sty	ME	VTMPAE + MG	VTMPAE + Sty	VTMPAE + ME
Density (in g/cm ³ at 20°C)	1.24	0.91	1.20	1.042	0.995	1.043
Viscosity (in cps at 20°C)	19.37	0.75	29.62	3301	3200	3312
Refractive Index	1.544		1.540	1.378	1.420	1.348

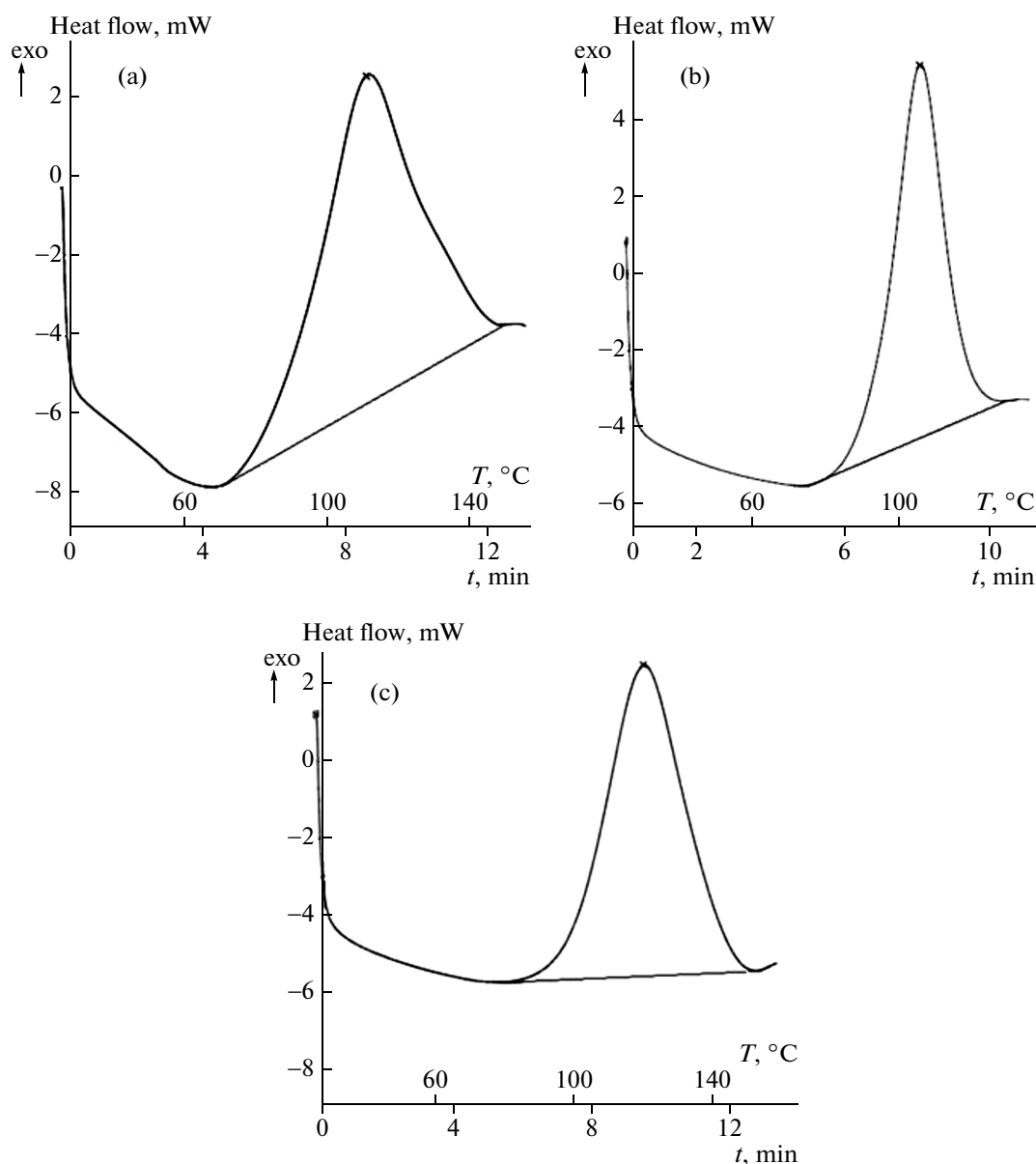


Fig. 9. Typical DSC for curing at 10 deg/min of vinyl ester resin samples (a) VTMPAE+Sty, (b) VTMPAE +MG, and (c) VTM-PAE+ME.

setting resins is one of the significant aspects in determining its end use. The thermal performance is greatly influenced by the physical structure, chemical composition and secondary interactions between the molecular chains etc. The thermal stability of the cured vinyl ester resins also depends on the number of functional groups present on the vinyl ester resins which further alter the physical structure and secondary interactions between the cured network systems. The MPA based vinyl ester resin samples (VTMPAE) containing methacrylated guaiacol (MG)/methacrylated eugenol (ME)/styrene as reactive monomers and benzoyl peroxide as free radical initiator have been evaluated for thermal stability in nitrogen atmosphere by thermo-

gravimetric analysis (TGA/DTG/DTA). The thermogravimetric (TGA) scans for isothermally cured samples of VTMPAE samples containing styrene, MG and ME as reactive monomers have been shown in Fig. 10. A noticeable single step mass loss in TG trace of VTMPAE containing methacrylated guaiacol (MG)/methacrylated eugenol (ME)/styrene as reactive monomers has been observed which indicates single step decomposition behavior of the cured VTMPAE samples. 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. T_{\max} can be taken as an indicator of extent of crosslink-

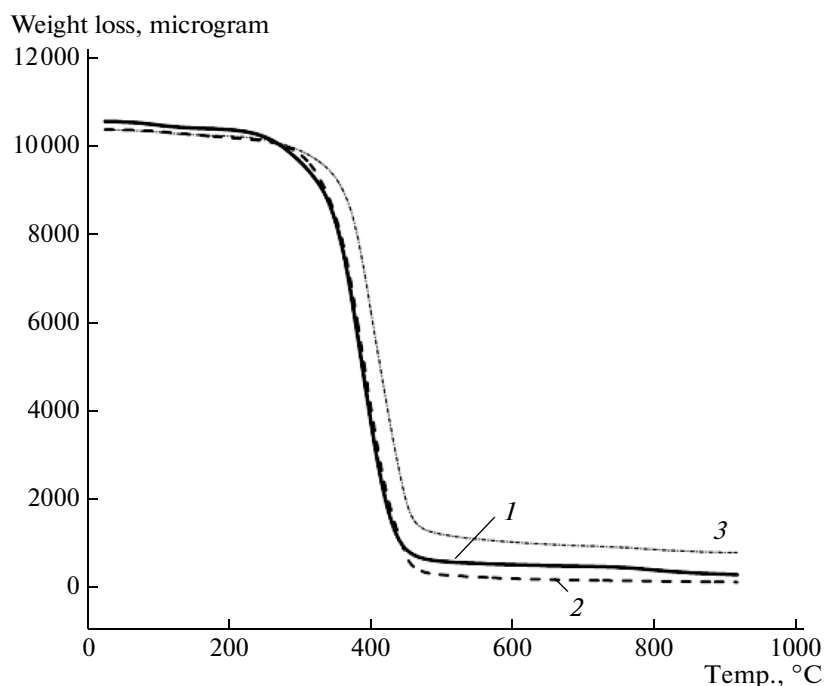


Fig. 10. TGA curves for cured vinyl ester resin samples (1) VTMPAE+Sty, (2) VTMPAE+MG, and (3) VTMPAE+ME.

ing in cured VTMPAE samples containing different reactive monomers. The T_{\max} are 380, 389 and 405°C for cured VTMPAE samples containing styrene, MG and ME respectively. On comparing the T_{\max} values from Fig. 10 and the temperatures at which 5, 10, and 20% weight loss occur in cured VTMPAE sample (Table 3), it can be confirmed that the VTMPAE samples cured using MG and ME are more thermally stable than that using styrene as reactive monomer. The reason for this can be attributed to increased degree of crosslinking of these cured VTMPAE samples which is due to the higher reactivity of the methacrylate group present in MG and ME monomers. The thermal stability of the sample containing ME is found to be even greater than that of MG, since the presence of the allyl group also increases the reactive sites which lead to better crosslinked network.

Table 3. Temperature at which occurs weight loss (in %) of cured VTMPAE samples containing styrene, MG and ME as reactive monomers, respectively during TGA studies

Weight loss, %	Temperature, °C		
	VTMPAE + ME	VTMPAE + MG	VTMPAE + STY
5	300	293	273
10	342	322	306
20	365	345	344

Evaluation of Mechanical Performance of VTMPAE Samples

From Table 4, it can be observed that the trimethylolpropane modified MPA based vinyl ester resin (VTMPAE) samples containing MG and ME as bio-based reactive monomers show better mechanical properties i.e. compression, flexural and tensile strength as compared to the VTMPAE samples containing styrene as reactive monomer. The mechanical behavior of the vinyl ester resin depends on the physical structure and chemical composition of the reactive monomers. Secondary interactions between the polymeric chains and higher degree of crosslinking for the cured vinyl ester resin system also affect the mechanical properties of the vinyl ester resin samples. The cured VTMPAE samples containing MG as reactive monomer show excellent tensile, flexural and compression strength as compared to the VTMPAE samples containing ME and styrene which may be attributed to higher reactivity of vinylic C=C of methacrylate group present in MG. Moreover, the increased polymeric chain interactions between the secondary hydroxyl group of VTMPAE and carbonyl group of MG due to intermolecular hydrogen bonding and polar attraction also tends to decrease the chain mobility and resist the deformation and VTMPAE matrix breakup. The mechanical performance of the sample containing ME is found to be lower than that of MG since the presence of two crosslinkable functionalities i.e. allylic group as well as methacrylic group in ME gave a highly crosslinked network, which

Table 4. The values of tensile, flexural and compression strength of VTMPAE samples containing styrene, MG and ME as reactive monomers

Sample name	Tensile strength, MPa	Flexural strength, MPa	Compression strength, MPa
VTMPAE + ME	46.70	73.20	37.60
VTMPAE + MG	53.56	81.55	41.72
VTMPAE + STY	42.09	66.51	31.35

in turn led to the brittleness in the samples and hence, deterioration of the mechanical performance of these samples as compared to the VTMPAE samples containing MG.

Evaluation of Chemical and Corrosion Resistance of Cured VTMPAE Resin Samples

Chemical and corrosion resistance studies have been performed as a function of % weight loss upon immersing the VTMPAE coated panels to chemical environment i.e. 1 M HCl, 1 M NaOH and 1 M NaCl solutions for 90 days. The data of chemical and corrosion resistance of VTMPAE resin samples containing styrene, MG and ME as reactive monomers have been reported in Table 5. It is evident from the table that cured VTMPAE samples containing ME shows high acid, base and salt resistance as compared to that of VTMPAE samples containing styrene and MG, which can be attributed to increased crosslinking of the VTMPAE sample network containing ME. The chemical and corrosion resistance of the VTMPAE samples

containing ME is found to be even greater than that of VTMPAE samples containing MG due to its potential ability to undergo copolymerization using two crosslinkable functionalities i.e. allylic group as well as methacrylic group.

Although cross linking is the most important structural aspect to prevent polymeric chains from dissolving in a solvent, the consequence of polarity and hydrogen bonding also cannot be ignored. Higher the degree of crosslinking, lesser will be free volume and segmental mobility in the polymeric chain array which prevents the permeation of the solvent molecules to crosslinked structure of VTMPAE samples containing ME.

Evaluation of Surface Morphology of Cured VTMPAE Resin Samples

The mild steel panels coated with cured VTMPAE resin samples (containing styrene, MG and ME as reactive monomers) taken for the chemical and corrosion resistance study by immersing the panels in different solutions i.e. 1 M HCl, 1 M NaOH and 1M NaCl for 90 days at room temperature are also examined for morphological or physical changes due to above chemical exposure with scanning electron microscopy (SEM). It is evident from the Fig. 11 that maximum surface deterioration or cracks have been observed on the surface of cured VTMPAE samples containing styrene as reactive monomer after chemical exposure to 1 M HCl, 1 M NaOH and 1 M NaCl respectively, whereas only roughness on surface of vinyl ester resin samples containing MG and ME as reactive monomers has been observed after chemical exposure which

Table 5. Chemical and corrosion resistance of VTMPAE samples containing Styrene, MG and ME

Solvent used	No. of days	Samples		
		Chemical resistance of VTMPAE + ME (in terms of wt % loss)	Chemical resistance of VTMPAE + MG (in terms of wt % loss)	Chemical resistance of VTMPAE + STY (in terms of wt % loss)
HCl	30	0.07	0.18	0.21
	60	0.25	0.45	0.61
	90	0.75	0.70	0.99
NaOH	30	0.29	1.09	1.89
	60	0.88	1.36	2.42
	90	1.18	1.67	2.82
NaCl	30	0.22	0.34	0.52
	60	0.27	0.49	0.59
	90	0.67	0.70	0.97

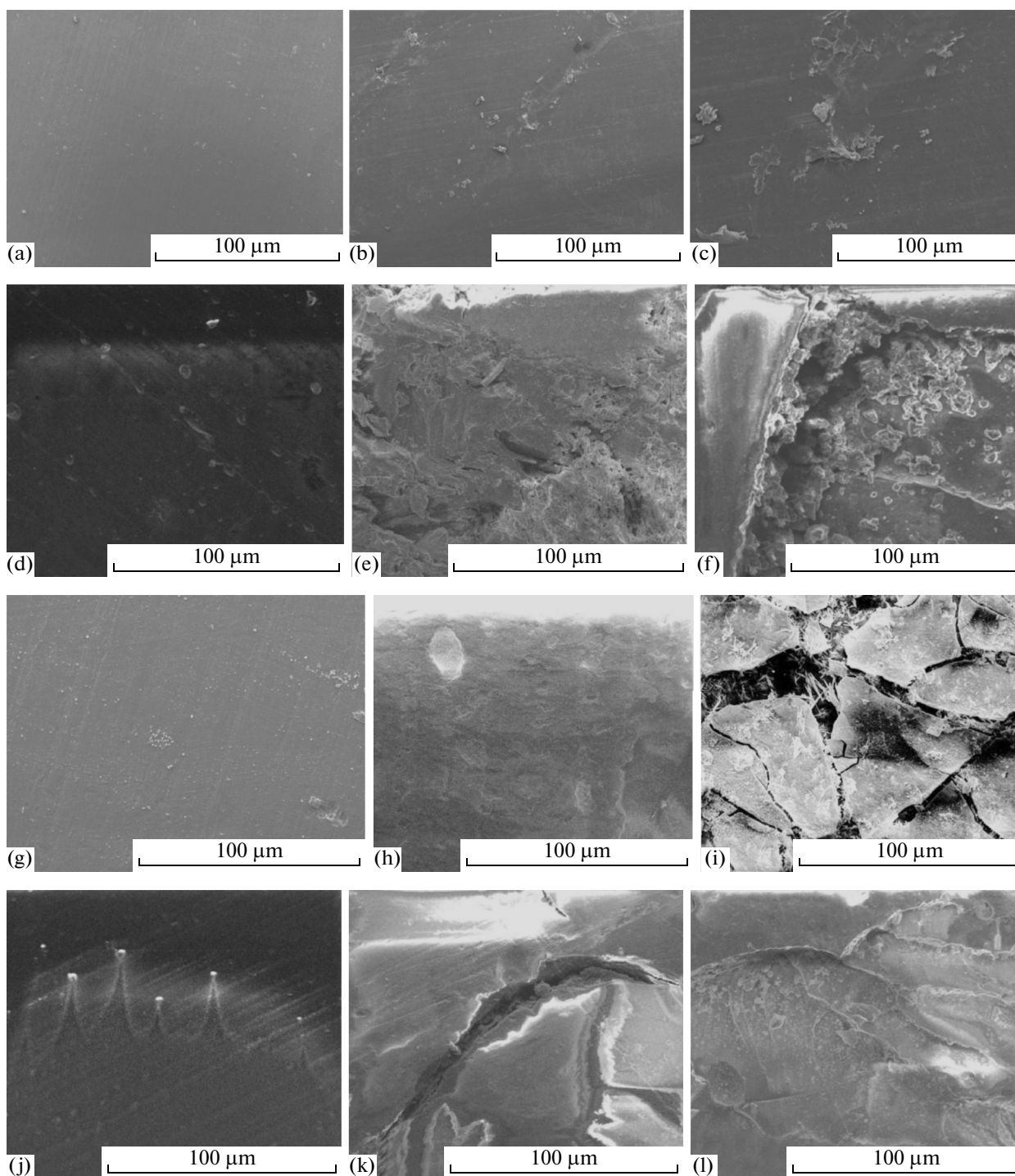


Fig. 11. SEM images of cured VTMPAE samples containing Styrene, MG, and ME as reactive monomers. (a–c) ME, MG, and Styrene (unexposed); (d–f) ME, MG, and Styrene (exposed to 1 M HCl); (g–i) ME, MG, and Styrene (exposed to 1 M NaOH) and (j–l) ME, MG, and Styrene (exposed to 1 M NaCl).

shows better chemical resistance of vinyl ester resin samples containing MG and ME than styrene and is in good agreement with % weight loss of the cured VTMPAE samples during the study of chemical and corrosion resistance behavior.

CONCLUSIONS

The present research article reports the findings of an experimental investigation on thermal, mechanical and environmental performance of bio-based multi-functional vinyl ester resin (VTMPAE) based on

Diels-Alder adduct of gum rosin and maleic anhydride (MPA) using methacrylated guaiacol (MG)/methacrylated eugenol (ME)/styrene as reactive monomers. The synthesis of MPA based vinyl ester resin (VTMPAE) and LMCs based reactive monomers i.e. MG and ME was confirmed using FTIR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The curing study of MPA based vinyl ester resin (VTMPAE) samples containing MG/ME/styrene as reactive monomers showed greater reactivity of LMCs based reactive monomers (MG/ME) towards VTMPAE as compared to that of petroleum based reactive monomer i.e. styrene. The VTMPAE samples containing MG/ME also showed better thermal stability and mechanical strength and better chemical and corrosion resistance in terms of % weight loss when exposed to different solutions of HCl, NaOH and NaCl than the samples containing styrene. The morphological studies of these chemically exposed samples also validate the weight losses (in %) occurred during the chemical and corrosion resistance studies. Consequently, the study in the research article indicated that the LMCs based reactive monomers i.e. MG and ME are excellent alternate to styrene. Thermal, mechanical and chemical performance of MPA based vinyl ester resin (VTMPAE) as high performance coatings materials were found to be comparable to those of conventional petroleum based coating materials. This suggests that gum rosin as monomer can open new avenues of synthesizing bio-based multifunctional vinyl ester resins as high performance coating materials and simultaneously addresses the environmental issues too.

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