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Synthesis, characterization of Mannich base oligomers used with epoxy resin for glass fibre-reinforced laminates

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Abstract This article aims to modify conventional epoxy resin by blending with four different Mannich base oligomers. These oligomers are similar to phenolic resin matrix and simultaneously function as amino curing agent for epoxy matrix. In this context, Mannich base oligomers were prepared, respectively, by Mannich polycondensation reaction of four phenols namely phenol, *m*-cresol, resorcinol and 1,5-dihydroxy naphthalene, respectively, with formaldehyde and piperazine in presence of acid catalyst. The resulting oligomers were characterized by elemental analysis, spectral studies (IR and NMR), number average molecular mass $\bar{M}_n$ estimated by non-aqueous conductometric titration and thermal stability by thermogravimetric analysis (TG). Each of these oligomers was used in resin matrix as a blending component for the modification of commercial epoxy resin for fabricating glass fibre reinforced laminates. Finally, these laminates were evaluated for their synergetic thermal stability, mechanical properties and chemical resistance to different reagents.

Keywords Mannich base · Oligomer · Curing agent · Epoxy · Blend · Laminate

Introduction

Epoxies are one of the most commonly used polymers in diversity of applications as reinforced composites in load bearing and aerospace materials. The requirements of high quality and high performance of reinforced composites have provoked a new fundamental research in the field of resin synthesis and curing systems. Consequently, over the last few decades, a great deal of work has been reported in the area of modification of conventional epoxy resin by preparing either blends or interpenetrating network of two different types of polymers or by chemical modification in chemical structure of conventional polymer. With reference to this, blending and curing of epoxy resin has been found as a successful method for polymeric material useful for industrial applications. [1–7].

In this context, Mannich bases are used as curing agents for epoxy resins much earlier than 2000 [8, 9]. Lin et.al have prepared a series of low molecular mass Mannich base products by Mannich polycondensation of phenol and its derivatives with formaldehyde and secondary amine and used in curing of epoxy resin. It was observed that such oligomeric Mannich base offered fast curing profile even at low temperature due to diversity of multiple functionalities of phenol and amine. Further, the resulting epoxy polymers showed enhanced flexibility and improved mechanical properties [10]. On the basis of this, the article has been undertaken with a view to investigate systematically the behaviour of Mannich base oligomers as a blending component structurally analogous to phenolic resin and simultaneously as amino curing agent in chemical modification of the epoxy resin matrix for glass fibre-reinforced composites. It includes the synthesis of Mannich base oligomers by polycondensation of four different phenols namely phenol, *m*-cresol, resorcinol and 1,5-dihydroxy naphthalene,

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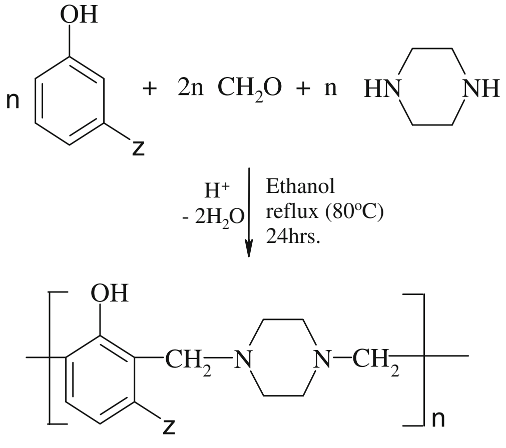
respectively, with formaldehyde and piperazine in acid medium. The resulting low molecular mass Mannich bases were preliminary characterized by their solubility behaviour, free phenol and free formaldehyde contents and number average molecular mass $\bar{M}_n$ The structure of these Mannich base oligomers were elucidated by elemental analysis, IR and NMR spectral studies. The thermal behaviour and isothermal curing of parent Mannich base oligomers and their corresponding blend with commercial epoxy resin was carried out in order to optimize the temperature for fabrication of glass fibre laminates. Glass fibre reinforced-laminates of epoxy resin–Mannich base as resin matrices were fabricated by hand lay-up method and subsequently characterized by their thermal stability, chemical resistance to different chemical reagents and mechanical properties such as flexural strength, impact strength, Rockwell hardness.

Experimental

All the chemicals used in this article were of analytical grade. 1,5-dihydroxy naphthalene and piperazine were purchased from Lancastar (UK) and Diamines chemicals Pvt. Ltd. (India), respectively. Commercial epoxy resin (EEW = 200) purchased from Sympol Ltd., Ahmadabad, India. Resorcinol and *m*-cresol were used after purification. Woven E—glass cloth used for reinforcement was purchased from Unnati Corporation, Ahmadabad, India.

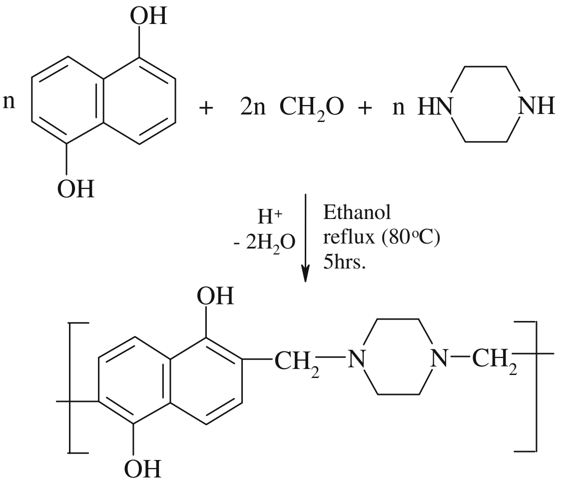
Synthesis of Mannich base oligomers

A solution phenol (0.2 mole) in 20 ml ethanol was charged to three-neck flask equipped with stirrer, reflux condenser and dropping funnel. To this, a solution of piperazine (0.2 mole) containing 1 ml conc. hydrochloric acid was added, and the reaction mixture was stirred for half an hour. It was cooled to 5 °C and 37% formalin solution (0.4 mole) was added drop wise and refluxed for 24 h. Finally, ethanol was removed under vacuum and resulting gummy mass was soaked in hydrochloric acid solution for overnight. It was neutralized by aqueous ammonia and filtered off. Unreacted formaldehyde, phenol and piperazine were removed by washing with water, followed by ether. Similar procedure was followed for the synthesis of other Mannich base oligomers from *m*-cresol, resorcinol and 1,5-dihydroxy naphthalene. They are designated as MP, MC, MR and MN for oligomer of phenol, *m*-cresol, resorcinol and 1,5-dihydroxy naphthalene, respectively. The general protocol of the reaction taking place in Mannich base polycondensation is shown in Scheme 1.



Where : Z = -H (MP), $-CH_3$ (MC), -OH (MR)

Synthesis of Mannich base oligomers (MP, MC, MR)



Synthesis of Mannich base oligomer (MN)

Scheme 1 Synthesis of Mannich base oligomer (MN)

Laminate fabrication

A typical method of fabrication of glass fibre reinforced laminates is given as follows: a suspension of commercial epoxy resin (20 g) and a Mannich base oligomer (20 g) was prepared in tetrahydrofuran (THF) was stirred for 5 min. This mixture was applied with a brush on 10 sheets of 200 × 200 mm woven glass cloth (E glass, 10 mill) and dried for 2 h. These 10 dried prepregs were stacked one over top of another and pressed between steel plates using Teflon sheet as mold releasing agent. It was then kept in an oven maintained at 160–170 °C temperature. Initially, normal contact pressure was applied and at the gel point, the plates were clamped to develop a pressure of 180 ψ for 4 h. The laminate so obtained was cooled to 50 °C before the pressure was released.

Measurements

The free phenol and free formaldehyde content of all Mannich Base prepolymers were estimated by the method reported in literature [11]. The C, H and N contents of these four oligomers were determined by means of Carlo Erba Elemental Analyzer (Italy). Number average molecular mass $\bar{M}_n$ of all Mannich base oligomers was determined by non-aqueous conductometric titration in pyridine as solvent and standard sodium methoxide in pyridine as titrant base. The $\bar{M}_n$ values of each oligomer was calculated according to the method reported in literature [12, 13] and shown in Table 1.

The IR spectra of Mannich base oligomers were scanned on Perkin Elmer Lambda-19 FTIR spectrometer using KBr cell. NMR spectra of MP, MC and MR were scanned on Hitachi, R-1500, 60 MHz. FT-NMR spectrometer in $CDCl_3$ using TMS as internal standard and that of MN oligomer was not obtained because of its insolubility in NMR solvents.

Thermal behaviour of each of the neat Mannich base oligomer and their blends with commercial epoxy resin was examined by thermogravimetric analysis. For this study, the TG of all the samples (8–15 mg) were carried out on a "Universal V2 60 TA" instrument by recording the thermogram in nitrogen atmosphere at the heating rate of 10 °C min^{-1} in the temperature range of 40–700 °C.

The mechanical properties and chemical resistance tests of glass fibre-reinforced laminates were estimated according to ASTM methods by cutting and machining the test specimens of the final dimensions. Flexural strength of the laminates was estimated according to ASTM D-790 on Instron testing machine at room temperature. The impact strength and Rockwell hardness of the glass composites were measured according to ASTM D 256 and ASTM D 785, respectively. Chemical resistance of laminate sample having dimension 25 mm × 1 mm was measured according to ASTM D 543 for 25% w/v NaOH, 25% v/v HCl and organic solvents.

Results and discussion

All of the four Mannich base oligomers were of white to brown colour powder. MP and MC are readily soluble in chloroform, DMF, DMSO and toluene, whereas MR and MN are partly soluble and insoluble in organic solvents respectively. Analytical data of these oligomers reported in Table 1 reveals approximately presence of 1% of free phenol and about 2–3% of free formaldehyde. The percent C, H and N contents of these oligomers are in agreement with calculated values based on proposed structure (Scheme 1). The estimation of average molecular mass $\bar{M}_n$ of these oligomers by non-aqueous conductometric titration indicates degree of polymerization (DP) 5–7 and the order in number average molecular mass $\bar{M}_n$ as MN > MR > MC > MP as expected on the basis of higher reactivity of resorcinol and 1,5-dihydroxy naphthalene.

IR structural studies of Mannich base oligomers have shown the characteristics vibrational frequencies corresponding to presence of three organic functional moieties namely phenolic, piperazine and bridge methylene group ($-CH_2-$) linking phenolic and piperazine moieties. The two characteristic features of phenolic functionality are a broad band in region 3,400–3,200 cm^{-1} due to O–H stretching vibration and a sharp peak around 1,240 cm^{-1} corresponding to C–O stretching vibration. The piperazine frequencies are observed near 1,100 and 1,080 cm^{-1} (N–C stretching) and in the range 1,480–1,440 cm^{-1} (aliphatic $-CH_2$ groups of ring). Finally, two weak bands at 2,960 and 2,820 cm^{-1} may due to the formation of methylene bridge between the phenol and piperazine. ^1H NMR spectra of three Mannich bases (MP, MC and MR) have shown the following characteristic proton signals. A multiplet appeared in the region of 5.8–7.5 δ value corresponds to aromatic protons of benzene ring. The three singlets are obtained at δ values of 8.4–8.8 (1H, –OH), 3.6 (2H, $Ar-CH_2$) and 2.6 (8H, piperazine ring). Further, one more singlet has observed at 2.2 due to (3H, $-CH_3$ of *m*-cresol) in ^1H NMR spectrum of MC oligomer. This concludes that the IR and

Table 1 Analytical data of Mannich base oligomers

Oligomer	Molecular formula of repeating unit	$\bar{M}_n$[a]	Free phenol/%	Free formaldehyde/%	Elemental composition/%					
					C		H		N	
					Found	Calc.	Found	Calc.	Found	Calc.
MP	$C_{12}H_{16}N_2O$	1,021	0.924	2.2	70.53	70.55	7.88	7.89	13.70	13.71
MC	$C_{13}H_{18}N_2O$	1,528	0.907	2.8	71.50	71.53	8.30	8.31	12.81	12.83
MR	$C_{12}H_{16}N_2O_2$	1,540	1.085	2.5	65.41	65.43	7.30	7.32	12.69	12.71
MN	$C_{16}H_{18}N_2O_2$	1,620	0.936	1.9	71.05	71.08	6.68	6.71	10.34	10.36

[a] $\bar{M}_n$ estimated by non-aqueous conductometric titration

Table 2 FT IR and ^{1}H NMR spectral data of Mannich base oligomers

Mannich base oligomer	FT IR frequencies/cm^{-1}								^{1}H NMR signals δ/ppm
	Phenolic moiety				Methylene bridge (–CH$_2$–)		Piperazine moiety		
	O–H stretching vibrations	O–H (in plane) bending vibration	O–H (out of plane) bending vibration	C–O stretching vibration	–CH$_2$– stretching vibration (asym.)	–CH$_2$– stretching vibration (sym.)	C–N–C (aliphatic) stretching vibration	–CH$_2$– bending vibration	
MP	3,428 (s,b)	1,347 (m,s)	758	1,254	2,928	2,820	1,130 (m) 1,090 (m)	1,456 (m)	2.6, (s) 8H piperazine ring 3.7, (s) 2H Ar–CH$_2$ 7.5–6.5 (m) 3H aromatic 8.8, (s) 1H O–H (hydroxyl proton)
MC	3,428 (s,b)	1,347 (m,s)	758	1,254	2,928	2,820	1,130 (m) 1,090 (m)	1,456 (m)	2.2, (s) Ar–CH$_3$ (3H) *m*-subst. –CH$_3$ 2.6, (s) N–CH$_2$ (8H) piperazine ring 3.6, (s) Ar–CH$_2$ (2H) 7.4–6.5 (m) O–H (hydroxyl proton) 8.4, (s) aromatic (2H)
MR	3,428 (s,b)	1,347 (m,s)	758	1,254	2,928	2,820	1,130 (m) 1,090 (m)	1,456 (m)	2.6, (s) N–CH$_2$ (8H) piperazine ring 3.6, (s) Ar–CH$_2$ (2H) 7.5–5.8 (m) O–H (hydroxyl proton) 8.7, (s) aromatic (3H)
MN	3,428 (s,b)	1,347 (m,s)	758	1,254	2,928	2,820	1,130 (m) 1,090 (m)	1,456 (m)	–

NMR data of Mannich base oligomers reported in Table 2 are in good agreement with our proposed structure shown in Scheme 1 and with the literature data [14].

Nowadays, thermogravimetric analysis (TG) is widely used for the thermal characterization of thermosets in quality control for investigations of thermal stability, kinetic study of thermal degradation reactions and the mechanism of curing. [15–22]. Therefore, the thermal behaviour of both parent unreinforced Mannich base oligomers and their epoxy blends cured in the ratio (1:1) was examined by TG. For this, thermal curing of unreinforced four blends of epoxy with each of the Mannich base oligomers (1:1) was carried out at 165 ± 3 °C for 4 h. These four cured blends were designated as EMP, EMC, EMR and EMN, respectively, for Mannich-based oligomer MP, MC, MR and MN. The resulting cured material was brittle and insoluble in all common organic solvents. The thermograms of these four Epoxy–Mannich base blends and Mannich base oligomers are shown in Figs. 1 and 2.

TG data of these samples reported in Table 3 reveals that both unreinforced Mannich base oligomer (MP and MC) and their epoxy blends (EMP and EMC) degraded in two steps with the mass loss of 97 ± 2% at 700 °C. The initial mass loss in the temperature range of 100–150 °C may be due to the presence of water. The value of this water content was found to be very small (2–4%) for MP and MC, whereas it was of significant amount (10 and 30%) for MR and MN, respectively, indicating hydrogen bond formation due to the presence of two phenolic groups. On the other hand, analogous initial mass loss due to water was decreased in TG of epoxy blends as expected on the basis of cured material. Onset of thermal degradation in each of cured blends and its parent Mannich base was occurred at almost same temperature but with higher rate of thermal degradation for parent Mannich base oligomer. Whereas that of blends was occurred over a wide range of temperature depending upon the curing nature of Mannich base oligomer as curing agent. The mode of thermal degradation of MP and MC oligomers was almost similar and can be explicable on the basis of presence of phenolic hydroxyl group. MR and MC oligomer were found thermally more stable because presence of two phenolic groups

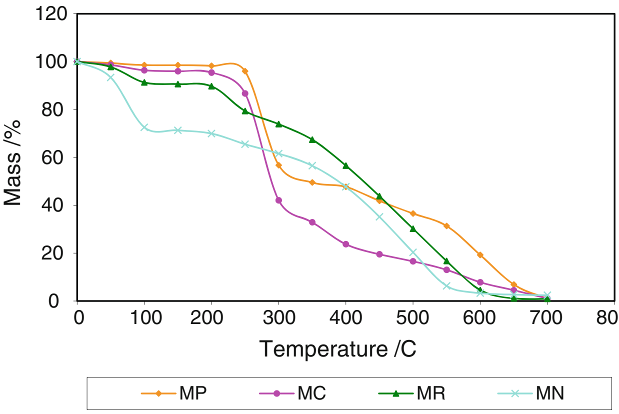


Fig. 1 Thermogram of Mannich base oligomers

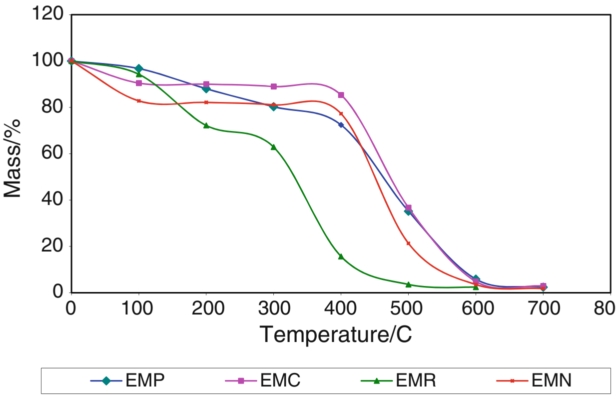


Fig. 2 Thermogram of epoxy:Mannich base oligomer blends

Table 3 TG data of Mannich base oligomer and its blends with epoxy resin

Oligomer and epoxy-oligomer blends	Percentage mass loss at different temperature/°C							T_0	T_{10}	PDT	IPDT	Char yield/%
	100	200	300	400	500	600	700					
Mannich base oligomer												
MP	1.47	1.78	43.28	52.31	63.46	80.77	99.07	23	275	300	564	0.93
MC	3.65	4.6	57.96	76.27	83.44	93.18	98.94	28	238	300	579	1.06
MR	8.72	10.3	26.14	43.46	69.85	95.48	99.13	2/8	190	520	825	0.87
MN	27.46	30.07	38.44	52.3	79.69	96.7	97.6	28	55	520	854	2.00
Epoxy resin–Mannich base oligomer blends												
EMP	2.42	5.79	34.51	72.42	80.26	87.98	96.67	32	241	350	600	3.33
EMC	2.93	4.90	37.37	85.26	89.01	90.02	90.49	31	253	350	520	9.12
EMR	2.43	3.57	15.35	62.83	72.10	84.15	94.15	32	279	350	575	5.85
EMN	1.89	3.53	21.31	77.22	81.07	82.16	82.80	32	293	350	518	16.92

may resulting into hydrogen bond formation. Similarly, the mode of thermal degradation in each of the cure blends was two-step processes, and each blend was thermally more stable than its parent Mannich base oligomer. All of these evidences of preliminary study of thermal stability by TG suggest the higher thermal stability of all four blends as compared to individual two components of blends (epoxy and Mannich base oligomer).

For the detail study of thermal degradation, TG data of four Mannich-based oligomers were normalized by the method reported in literature [23] for estimation of thermal parameters T_0, T_{10}, PDT (procedural decomposition temperature) and IPDT (integral procedural decomposition temperature). According to this method, the thermal stability of Mannich base oligomer was estimated in terms of PDT, IPDT by the equation.

$$\mathrm{IPDT} = T_\mathrm{i} + \frac{\text{Total area of thermogram}}{\text{Area under the thermogram}}(T_\mathrm{f} - T_\mathrm{i})$$

where, T_i = initial temperature, T_f = final temperature.

These data of T_0, T_{10}, PDT and IPDT of thermal decomposition shown in Table 3 indicate the temperature range for the first and second steps of degradation as 200–300 and 350–700 °C, respectively. These two steps of degradation of Mannich based oligomers can be explained as first step of the degradation may be the removal of aliphatic piperazyl group linked to phenolic part in the Mannich base oligomers. The observed mass loss corresponding to this piperazyl group was 49 (48), 54 (53), 47 (45) and 37 (35), respectively, for MP, MC, MR and MN, and it is also found in agreement with calculated mass loss. The second step of the degradation may be due to decomposition of phenolic component and gives about 97 ± 2% mass loss at 700 °C. This is further in agreement with data of char yield as it increases with increase in molecular mass of phenolic group of Mannich base from MP to MN. On the basis of these probable steps of thermal degradation of Mannich base, the protocol of the thermal degradation can be shown as given in Scheme 2.

Comparison of flexural strength of all the laminates with that of commercial epoxy-based laminates has indicated positive synergistic effect due to higher number of curing sites yielded highly crosslinked materials. Besides this, the values of flexural strength of the four laminates are in good agreement with those of the reported value for epoxy cured material by using Mannich base derived from bisphenol-A, poly(oxyalkylene) diamine and formaldehyde [24–26]. The estimated impact strength of first three laminates (MP, MC and MR) has shown a decrease in impact strength and to some extent which may be due to partial aliphatic nature of Mannich base polymers. Lastly, Rockwell hardness in the range of 75–100 is comparable to that of laminates of commercial epoxy (Rockwell hardness = 79). Examination of chemical resistance test reveals that all laminates have good resistance to organic solvent and concentrated HCl (25% v/v) but the concentrated alkali (25% w/v) causes changes in their thickness and mass to about 1% (Table 4).

Scheme 2 Protocol of thermal degradation of Mannich base oligomers

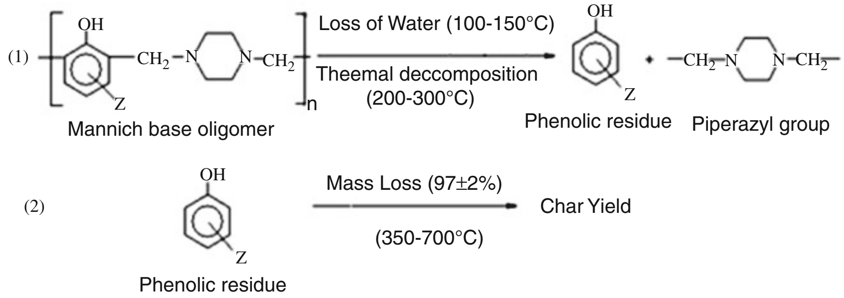


Table 4 Chemical resistance, mechanical and electrical properties of laminates (resin system: epoxy resin–Mannich base oligomer)

S No	Resin system for laminates[a]	Chemical resistance[b]/% change)		Flexural strength/MPa	Rockwell hardness/M scale	Izod impact strength/J m^{-1}	Electrical strength in air/kV mm^{-1}
		Thickness	Mass				
1	Epoxy resin	0.7	1.3	554.14	79	500	18.5
2	Epoxy-MP	0.4	0.9	618.24	72	590	19.5
3	Epoxy-MC	0.5	1.0	633.43	65	614	20.2
4	Epoxy-MR	0.3	1.2	656.84	78	629	20.3
5	Epoxy-MN	0.4	1.1	673.63	75	638	20.8

[a] Reinforcement: 'E' type glass cloth, ten layers, laminate size: 200 mm × 200 mm × 1.87 mm

[b] Chemical resistance to 25% w/v NaOH: composites are unaffected by organic solvents and 25% v/v HCl

Conclusions

The systematic investigation of modification of epoxy by blending with Mannich base oligomeric product yields as better polymer matrix with better mechanical properties and of higher thermal stability as compared to that of epoxy resin cured with diamines. Hence, they can be used in end use applications for engineering materials where epoxy resin has been used as matrix glass fibre laminates.

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