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Enhanced thermal stability and mechanical performance of epoxy resin with amine-terminated aromatic amide oligomer: unveiling the ring-opening curing phenomenon

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Abstract

Amine-terminated aromatic amide oligomer (ATAAO) was used to cure diglycidyl ether of bisphenol A epoxy resin. P-phenylenediamine (PPDA) and isophthaloyl chloride (IPC) underwent a condensation reaction to synthesize the oligomer using dimethyl acetamide (DMAc) as the solvent. The successful synthesis and semi-crystalline nature of oligomer was confirmed using ¹HNMR, FT-IR, and X-ray diffraction, respectively. The curing reaction was carried out by mixing ATAAO and diglycidyl ether of bisphenol A (DGEBA) epoxy resin in DMAc, followed by curing at 363.15 K and 393.15 K for 30, 60, 90 and 120 min, respectively. Moreover, the ring-opening curing phenomenon in epoxy was confirmed by ¹HNMR and FT-IR. XRD analysis revealed the amorphous nature of the cured epoxy. Thermal analysis revealed an increase in thermal stability (553.21 K to 580.32 K) and glass transition temperature (423.21 K to 481.61 K) with increasing curing temperature (363.15 K to 393.15 K) and curing duration (30 min to 120 min). Stress–strain analysis revealed an increase in Young's modulus (5.93 MPa to 41.09 MPa) and stress at the break (7.79 MPa to 31.92 MPa) of cured epoxy films with changing curing conditions. Moreover, a homogeneous surface of cured epoxy films containing slight bumps and small globular without any phase separation was observed in scanning electron micrographs.

Keywords DGEBA · Extent of curing · FT-IR · Tensile properties · Thermal stability

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Abbreviations

ATAAO	Amine terminated aromatic amide oligomer.
PPDA	P-phenylenediamine
IPC	Isophthaloyl chloride
DMAc	Dimethyl acetamide
¹ HNMR	Proton-nuclear magnetic resonance
FT-IR	Fourier transform infrared
DGEBA	Diglycidyl ether of bisphenol A
MTHPA	Methyl tetrahydro phthalic anhydride
NA	Nadic anhydrie
ODA	Oxydianiline
HDA	Hexmethylenediamine

Introduction

Curing is a process wherein functional groups present in a polymer react in such a way as to produce a crosslinked three-dimensional network which ultimately leads to the preparation of a hard, infusible and rigid material with enhanced properties and applications. [1-3]. The curing of epoxy resins, and conversion of epoxide groups, is mainly done by adding curing agents or curing catalysts. The curing agents are polyfunctional compounds such as aliphatic or aromatic amines, carboxylic acids, anhydrides, Lewis's acids, and polyamides that are used with an epoxy resin in a definite stoichiometric ratio, whereas the curing catalysts are monofunctional compounds that are responsible to selfpolymerize the epoxy resin and are always used in much lower amounts than the stoichiometric ratio, e.g., metal salts complexes and ammonium and phosphonium salts [4-6]. Kexin and his co-workers studied the effects of different anhydride curing agents such as nadic anhydrie (NA) and methyl tetrahydro phthalic anhydride (MTHPA) on the thermomechanical properties of diglycidyl ether of bisphenol A (DGEBA). They claimed that the DGEBA/NA system had a greater glass transition temperature (T_o) and Young's modulus than the DGEBA/MTHPA system [7]. Moreover, the effect of 12 different amine curatives on the curing of DGEBA coatings was investigated in 2021 wherein researchers also compared the curing regime and performance of DGEBA coating with an epoxy synthesized from eugenol [8].

The epoxy resin can be used in a wide range of products, such as adhesives, bridge coatings, automotive primers, electrical insulation materials, dental bonding agents, flame retardants, wall panel coatings, flooring, glues, laminates, inks, paints, model making, and primers, plastic products, surface coatings, and varnishes [9–11]. Moreover, it also works as an encapsulating agent and finds potential application in preparing diverse composite materials [12–14]. However, the curing process significantly influences the strength of adhesive joints and composites formed with epoxy [15–17]. In this context,

Luo et al. investigated the effect of curing temperature on the thermomechanical, morphological, and mechanical properties of DGEBA epoxy-poly (*ɛ*-caprolactone) blends. Additionally, they discussed the effects of temperature changes on phase separation in cured epoxy above and below the melting point (T_m) of poly (ε -caprolactone) [18]. Zahra et al. cured DGEBA epoxy with amine-type oligomers synthesized by the polycondensation reaction of isophthaloyl dichloride with oxydianiline (ODA) and hexmethylenediamine (HAD). They also investigated the morphological, structural, and mechanical features of the cured epoxy systems wherein epoxy cured with the oligomer synthesized from ODA posed higher thermal and mechanical values than the oligomer prepared from HAD [19]. Another research examined the curing procedure and mechanical characteristics of DGEBA epoxy resin using primary amine as a curing agent in various ratios [20]. Different amino acids have also been utilized as curing agents for DGEBA epoxy resin in many studies wherein the results highlighted the significant impact of curing agents' structure and curing conditions on the thermo-mechanical properties of the epoxy [21-23]. Huang et al. used low molecular weight polyamide as a curing agent to improve the thermal and mechanical properties of epoxy resin [24]. Recently, researchers have also investigated ionic liquids as curing agents to cure the epoxy resins at different curing conditions [25, 26].

Numerous investigations have demonstrated the critical role of curatives and curing conditions in improving the various properties of the DGEBA epoxy [15-20, 27]. Moreover, various studies explained the role of aliphatic amines as curing agents for epoxies at specific temperatures and duration. However, there is a limited study about the use of amine-terminated aromatic amide for curing DGEBA epoxy while varying curing temperature and time. Therefore, an effort has been made here to explore the effect of curing temperature and duration on the curing of DGEBA epoxy by employing the synthesized ATAAO. Amine-terminated aromatic amide oligomer is preferred among other curatives for epoxy curing due to its stability, and superior thermal, mechanical and solvent-resistant properties [19, 20, 27]. The ATAAO cured epoxy was characterized by a Fourier transform infrared spectrometer (FT-IR), proton nuclear magnetic resonance (¹HNMR) spectrometer, x-ray diffractometer (XRD), scanning electron microscope (SEM), thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC), and universal testing machine (UTM) for the evaluation of structural, morphological, thermal and tensile properties.

Experimental

Fig. 1 Synthesis of amine-

Materials

Isophthaloyl chloride (IPC; Fluka, 98%), p-Phenylenediamine (PPDA; Aldrich, 97%), anhydrous N, N'-dimethylacetamide (DMAc; Aldrich, 98.8%), triethyl amine (TEA; Fluka, 98.9%), and methanol (Aldrich, 99%) were employed as received for the synthesis of ATAAO. To determine the viscosity and average molecular weight of the synthesized ATAAO, the oligomer was dissolved in H_2SO_4 (Scharlau, 96%). Moreover, the epoxy used in this investigation was DGEBA with 221 g/epoxide equivalent weight (EEW).

Synthesis of amine-terminated aromatic amide oligomer (ATAAO)

Utilizing low-temperature condensation polymerization, 3 mol of PPDA and 2 mol of IPC undergo a reaction to synthesize ATAAO [28]. For a typical synthesis, the weighed amount of PPDA was taken in a quick-fit conical flask with an accuracy of ± 0.0001 g and dissolved in anhydrous DMAc with continuous stirring at room temperature. The conical flask, containing completely dissolved PPDA, was placed inside a chilling unit and the temperature of the unit was maintained at 278.15 K. The chilling unit consisted of a sealed stainless-steel box with inlet and outlet ports for circulation of the chilled liquid wherein methanol was used as a coolant. Then, a weighed quantity equivalent to 2 mol of IPC was taken in a beaker with an accuracy of ± 0.0001 g and dissolved in anhydrous DMAc. The dissolved IPC was poured into a dropping funnel coupled with a PPDA-containing conical flask. The dropping funnel valve was open while adjusting the flow of IPC solution at a speed of one drop per minute to transfer it into the PPDA solution for condensation reaction under vigorous stirring till the completion of the reaction. The formed HCl during the condensation reaction was scavenged as a white precipitate of triethyl ammonium chloride by adding triethylamine (TEA). The white precipates were filtered out whereas the filtrate, which contained the required oligomer, was further treated with methanol to precipitate the ATAAO. The precipitates were washed with methanol and water and then dried in a vacuum pump for 48 h at 333.15 K. The chemical reaction for the synthesis (Scheme 1) of ATAAO from its monomers is given in Fig. 1.





Triethylamine

Triethylamonium chloride

Curing of DGEBA Epoxy

In this study, 0.014 mol of DGEBA were dissolved in DMAc, and then 0.014 mol of ATAAO were added to the epoxy solution at room temperature and stirring was continued till the formation of a homogeneous solution followed by the pouring of solution into a Teflon petri dish. The petri dish was kept in a desiccator, that was attached to a vacuum pump, at 333.15 K for twelve hours to remove air bubbles and solvent. The dried sample was then shifted to the oven for studying single-step curing at 363.15 K for 30 min. A similar procedure (Scheme 2) was adopted to cast the other seven films at different curing conditions mentioned in Table 1. The cured films were then removed from the petri dishes and labeled summarized in Table 1. The thickness of the films was found to be 0.45 ± 0.02 mm using a screw gauge.

Characterization

The synthesized materials were characterized with 400 MHz NMR (Bruker Corporation, Billerica, Massachusetts, United States), Nicole Nexus 470 FTIR (Thermo Fischer Scientific, Waltham, Massachusetts, United States), and 3040/60 X'Pert PRO XRD (PANalytical, Almelo, the Netherlands). SDT Q600 TGA/DSC analyzer (TA instruments, New Castle, Delaware, United States) was used to obtain the thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of the cured epoxy samples at a heating rate of 20 K/min from 298.15 K to 873.15 K in a nitrogen environment. The tensile analysis of cured epoxy was performed on an M500-30CT universal testing machine (Testometric Co.Ltd., Rochdale, United Kingdom) using American Society for Testing and Materials (ASTM) standard D-882. Moreover, the surface morphology of the partially (EA-1) and completely (EA-8) cured epoxy films were also evaluated using a JSM-6490LA

Table 1 Curing conditions and labeling of films

Curing Conditions		Film Label		
Temperature (K)	Duration (min)			
363.15	30	EA-1		
363.15	60	EA-2		
363.15	90	EA-3		
363.15	120	EA-4		
393.15	30	EA-5		
393.15	60	EA-6		
393.15	90	EA-7		
393.15	120	EA-8		



Scheme 1 Schematic route for the synthesis of amine-terminated aromatic amide oligomer



Scheme 2 Schematic route for the preparation of amine-terminated aromatic amide oligomer cured DGEBA epoxy resin

scanning electron microscope (JEOL Ltd., Akishima, Tokyo, Japan).

Results and discussion

Proton NMR Spectroscopy

The chemical structure of the ATAA oligomer and the curing mechanism of DGEBA epoxy resin with the synthesized oligomer were confirmed by ¹H-NMR. Moreover, the position of different protons in the oligomer is provided in Fig. 2, whereas Fig. 3a-c shows the proton NMR spectra of the ATAA oligomer and uncured and cured epoxy resins, respectively. In Fig. 3a, the peak at 2.5 ppm is attributed to the DMSO-d6 solvent, and the peaks responsible for aromatic amide appear in the 6.6–8.5 ppm range.

Considering the above chemical structure, the terminated amino protons "a" appeared as a broad band from 3.2–3.7 ppm because of the quadruple moment and hydrogen bonding [29]. The doublet at 6.6 ppm is due to "b" protons. These are the ortho protons of the aromatic ring directly attached to the amino group. Since the shielding effect is dominant at the ortho position, therefore, these are upfield compared to other aromatic protons. The 7.4–8.5 ppm peaks are due to various aromatic protons (c, d, e, f, and g). The appearance of small broad bands at 10.1 and 10.5 ppm are attributed to the amide protons (h and i), respectively. These broad bands are due to hydrogen bonding in the molecular backbone and the quadruple moment. Two singlets that appear at 2.8 and 2.9 ppm are unidentified.

The representative ¹H-NMR spectra of the uncured and cured epoxy were recorded and presented in Fig. 3a and b, respectively. The glycidyl terminal group in uncured epoxy is characterized by two fine peaks in the chemical shift (δ) range of 2.68–2.84 ppm. Another tiny band at 3.41 ppm is observed due to the small hydroxyl moiety in uncured epoxy. Therefore, the glycidyl terminal group peaks in the chemical shift range of 2.68–2.84 ppm corresponds to the epoxy ring protons used to study the epoxy curing via the ring-opening mechanism. A sharp singlet at 1.58 ppm is due to the methyl protons in uncured epoxy resin. When a reaction between the epoxy ring's electrophilic carbon and aromatic amide's nucleophilic amine took place, the epoxy ring proton peak disappeared, as shown in Fig. 3c. Therefore, in the ¹H-NMR spectrum of ATAA oligomer-cured epoxy film, a doublet at

2.55 ppm is observed due to methylene protons of the epoxy ring moiety generated after the ring-opening reaction.

A singlet at 1.75 ppm is attributed to the methyl protons of the epoxy that appeared in the cured sample. The OH proton in uncured epoxy appeared at 3.41 ppm, however, a broad range of 3.69-4.65 ppm is occupied by broad signals of OH protons after curing as shown in Fig. 3c. The environment of these protons is different because there are OH protons of parent epoxy and OH protons obtained after opening the oxirane ring. The doublets of various aromatic protons appeared at 6.84–7.14 ppm whereas in cured epoxy, these protons are observable in the range of 6.95–7.92 ppm. Moreover, the peak at 10.40 ppm is attributed to the D_2SO_4 . Consequently, the disappearance of terminal epoxy doublet and the appearance of multiple peaks corresponding to hydroxyl and other aliphatic protons in the ¹H-NMR spectrum of cured epoxy confirm the curing of epoxy resin via a ring-opening mechanism. Moreover, the presence of characteristics peaks with their respective chemical shifts in ATAA oligomer and uncured epoxy resin, and the disappearance/ shift of characteristics peaks observed in the cured epoxy resin are given in Table 2.

Structural evaluation using FTIR analysis

FT-IR analysis of amine-terminated aromatic amide oligomer, uncured and cured epoxy films was conducted to study the changes in IR absorption bands before and after the curing reaction. The vibrational bands in oligomer, uncured, and cured epoxy were assigned, and compared with the help of literature values as shown in Fig. 4 [28]. In Fig. 4a, the intensity of primary amine bands, which usually appeared at $3400-3371.6 \text{ cm}^{-1}$ in the p-phenylenediamine (PPDA) spectrum, significantly decreased due to the formation of amide linkage in the oligomer [30]. Therefore, the broadband in the spectrum of oligomer at 3273.4 cm^{-1} corresponds to the N-H bond stretching of both secondary amide and primary amines, which generally lie in the range of 3500-3200 cm⁻¹. Usually, primary amines show two bands in this region. However, in some cases, when primary amine moieties are less than secondary amines, single broadband appears due to both secondary and primary amine stretching. An intense amidic carbonyl stretching band appeared at 1640.8 cm⁻¹ and many weak bands appeared in the range of 3070–2600 cm⁻¹ corresponding to the extending of aromatic C-H bonds. Some intense bands

Fig. 2 The representative chemical structure of ATAA oligomer with designated positions of different protons



Fig. 3 The representative ¹H-NMR of (**a**) ATAA oligomer, (**b**) uncured epoxy and (**c**) oligomer cured DGEBA epoxy resin. The different colors (red, blue, green, and yellow) show the type of protons present in the spectrum and their respective chemical structures



Table 2¹H NMR data of theuncured epoxy, oligomer, andoligomer cured epoxy

Sr.#	Proton	Uncured epoxy resin (δ ppm)	Oligomer (δ ppm)	Cured epoxy resin (δ ppm)		
1	Terminal amine	_	3.2–3.7	Disappear		
2	Amide	_	10.11 and 10.49	Disappear		
3	Aromatic	6.84-7.14	6.57-8.54	6.95-7.92		
4	Epoxy ring	2.68-2.84	_	Disappear		
5	Methyl	1.58	_	1.75		
7	Hydroxyl	3.41	_	3.69-4.65		

appeared in the range of $1605.4-1401.2 \text{ cm}^{-1}$ due to the C=C and C-N bond widening of aromatic rings, and the bands in the range of $1350-1000 \text{ cm}^{-1}$ are most probably due to the phenyl-C-N stretching and because of the interaction between N–H winding and C-N stretch of the C-N–H (1252.4 cm⁻¹) groups.

The uncured DGEBA epoxy resins FTIR spectrum is shown in Fig. 4b, and Table 3 presents the different absorption bands for CH_2 and CH_3 , Ar-C=C-H bending, epoxy CH₂-(O- CH-) ring extending vibration and -C-Ar-O-C stretching. The presence of epoxy groups was verified due to the existence of absorption bands at 3,056.6 and 913.5 cm⁻¹. In diglycidyl ether of bisphenol A-type epoxy, a bending band originating from the epoxy ring was observed at 913.8 cm⁻¹. Two stretching bands of aliphatic C-O were observed at 1031 and 1181.6 cm⁻¹. An intense phenyl-O band was observed at 1228.4 cm⁻¹, and three C-C extending bands of the aromatic nucleus were observed at 1506.4, 1581.1, and 1606.1 cm⁻¹. Three bands of aliphatic C-H stretching were noticed at 2870.4, 2926.5, and 2964.7 cm⁻¹, while the epoxy group stretching band was observed at 3056.6 cm⁻¹. Finally, a broad O-H extending band was detected at 3505 cm^{-1} .

However, after the epoxy curing reaction, few IR vibrations related to epoxy group disappeared, and the increase in the intensity of the O–H stretching band was noticed due to the formation of few more OH groups, as shown in Fig. 4c. Therefore, the disappearance of these IR absorption bands ascertains the curing of diglycidyl ether of bisphenol A-type epoxy resin as a result of curing with amine-terminated aromatic amide oligomer. The disappearance of terminal epoxy ring bands and the appearance of hydroxyl and some aliphatic bands are presented in Table 3, which confirms the curing of epoxy resin via the ring-opening mechanism.

The extent of curing by FTIR Spectroscopy

The partial IR spectra in Fig. 5 represent a gradual decrease in the epoxy ring peak (913 cm⁻¹) with a decrease in curing temperature and time. The extent of curing (α_{IR}) was determined using the following equation by calculating the peak area of the epoxy ring peak that appeared at 913 cm⁻¹ [31].

$$\alpha_{IR} = 1 - \frac{A_t}{A_o} \tag{1}$$

where " A_t " is the peak area after a certain time (t) and " A_o " is the peak area at time zero.

Figure 5 shows that the extent of epoxy conversion increases with an increase in curing duration at 363.15 and 393.15 K, respectively. Wherein, a faster epoxy conversion $(\sim 86\%)$ was noticed in the first 60 min. in comparison to the final 60 min at 363.15 K curing temperature. Whereas at 393.15 K curing temperature, ~94% epoxy conversion was observable in the initial 30 min. which was further approached to ~ 100% conversion during 120 min. of curing as shown in Table 4. A greater extent of curing was also observed by a few researchers with increasing curing temperature even at the same curing time [32, 33]. This increase in the extent of epoxy conversion at higher temperatures can be attributed to the availability of sufficient activation energy to enhance the reaction kinetics whereas longer curing duration may help in the completion of the cross-linking reaction.

XRD analysis

Figure 6 presents the XRD pattern of the ATAAO and cured epoxy wherein five diffractions were observed for the oligomer at 20 values of 18.04, 20.91, 24.57, 28.05, and 41.34 with d-spacing 4.92, 4.25, 3.62, 3.18, and 2.18 Å, respectively. These diffractions show some crystallinity in the structure of the oligomer that can be due to the para and meta linkages. Whereas a broad peak appears in the XRD pattern of cured epoxy describing the amorphous nature of the ATAAO-cured epoxy. It is worth noting that during the curing, the cross-linking reaction between ATAAO and epoxy disrupts the existing crystalline nature of the oligomer.

Thermal analysis

The thermogravimetric curves of the ATAAO-cured epoxy films are presented in Fig. 7. Where a single-step decomposition was observed for all cured samples. The slow weight Fig. 4 The representative FTIR spectra of (a) ATAA oligomer, (b) uncured epoxy, and (c) oligomer cured DGEBA epoxy resin



loss in the first part of the TG curves till 530 K is attributed to the evaporation of moisture and solvent present in the samples. This loss was found relatively greater in the sample cured at 363.15 K for 30 min in comparison to other samples. Moreover, the initial degradation temperature (T_{onset}) and temperature at 10% weight loss (T_{10}) were considered (Table 5) to estimate the thermal stability of the cured samples. The initial degradation in cured epoxy is mainly attributed to the breakage of side chains and oligomeric content [34, 35]. Above 580 K in the completely cured sample (EA-8), a rapid decomposition due to the major chains of the epoxy while producing volatile gases was observable with maximum degradation at ~ 672 K. However, the remaining material was decomposed between ~ 700 K and ~ 875 K as

Table 3FTIR data of theuncured epoxy, oligomer, andoligomer cured epoxy

Sr.#	Functional group description	Uncured epoxy (cm ⁻¹)	Oligomer (cm ⁻¹)	Cured epoxy (cm ⁻¹)
1	Broad O-H stretching band	3505 weak	-	3315-3290 strong
2	Epoxy ring stretching band	3056.6	-	Disappear
3	Aliphatic –CH and –CH ₂ bands	2964.7, 2926.5 and 2870.4	-	2954,2920.5 and 2851
4	Intense phenyl-O band	1228.4	-	1217.7-1227.9
5	Aliphatic C-O stretching bands	1031. 3 and 1181.6	-	1030 and 1180.4
6	Epoxy ring bending band	913.5	-	Disappear
7	Aromatic $-C = C-H$ stretching band	1606.1	1605.4	1605.1-1605.8
8	Broad band of -NH stretching	-	3273.4	-OH overlay
9	Secondary amides -NH bending	_	1562.7	Disappear
10	-OH bend	-	-	1643.1-1646.7

Fig. 5 The partial FTIR spectra of uncured (E) and ATAAO cured epoxy resins (EA-1 to EA-8) at (**a**) 363.15 K and (**b**) 393.15 K curing temperatures



Table 4	Extent of conversion
of the ep	poxy group at different
curing t	emperatures and curing
times	

Curing Temperature									
363.15 K				393.15 К					
Sample Code	Curing Time (min)	A _t	α_{IR}	$\% \alpha_{IR}$	Sample Code	Curing Time (min)	A _t	α_{IR}	$\% \alpha_{IR}$
EA-1	30	1.30	0.6438	64.38	EA-5	30	0.22	0.9397	93.97
EA-2	60	0.51	0.8603	86.03	EA-6	60	0.16	0.9562	95.62
EA-3	90	0.47	0.8712	87.12	EA-7	90	0.0065	0.9982	99.82
EA-4	120	0.36	0.9014	90.14	EA-8	120	0.0042	0.9988	99.88

shown in Fig. 7. Moreover, $T_{00,set}$, $T_{10,set}$, $T_{10,set}$ and T_{max} were estimated and presented in Table 5. The almost completely cured epoxy (EA-8) was observed stable up to ~582 K with ~625 K T_{10} value whereas EA-1 was thermally stable till ~553 K with significantly lower T_{10} value i.e. ~520 K. The T_{10} and $T_{00,set}$ values present the thermal stability of the

EA-8 sample among other samples. The rise in temperature corresponding to initial degradation and 10% weight loss of the epoxy resin are the evidence for an increased thermal resilience with increasing curing temperature and duration. This difference was attributable to an increase in crosslinking density due to prolonged curing, which



Fig. 6 The representative diffraction patterns of (a) ATAA oligomer and (b) oligomer cured DGEBA epoxy resin



Fig. 7 The thermogravimetric (TG) curves of ATAAO cured epoxy samples (EA-1 to EA-8)

produced a network that was more precisely crosslinked and matched the results of the FTIR investigation. Moreover, the glass transition temperature (T_o) was also estimated for the samples from the curves obtained through differential scanning calorimetry (DSC) as shown in Fig. 8. Wherein, EA-8 sample posed a higher T_g value in comparison to partially cured samples. This increase in T_o values with increasing the curing temperature and duration is attributed to the higher degree of cross-linking which ultimately restricts the movement of chains in the rigid 3D epoxy network [36, 37]. Previously, different amino acids were used as curing agents to cure DGEBA epoxy, wherein, L-tyrosine posed a significant role in improving the T_g (~461.45 K) of the epoxy [21]. Jeyranpour and coworkers also reported a higher T_{σ} (~455 K) value of DGEBA epoxy cured with diethyltoluene diamine (DETDA) as compared to the epoxy cured with triethylenetriamine (TETA) curing agent [38]. Another study revealed the higher thermal stability (~583.15 K) of DGEBA epoxy resin cured with m-Phenylene diamine (mPDA) [39]. Moreover, Baig et al. reported the higher thermal stability (~645.15 K) of DGEBA epoxy resin cured by amine-terminated aromatic amide oligomer synthesized using oxydianiline and isophtahloyl chloride as compared to amine-terminated aliphatic amide oligomer prepared by mixing hexamethylenediamine and isophtahloyl chloride [19].

Stress-strain analysis of cured epoxy films

Stress-strain curves of ATAAO cured epoxy films are shown in Fig. 8. To assess the tensile properties of the cured epoxy films through representative stress-strain curves, rectangular strips of $40 \times 7 \times 0.05$ mm³ dimensions were stretched at a crosshead speed of 2 mm/min at room temperature as per ASTM D-882 and three measurements were averaged for each sample. Except for EA-1 (Fig. 9a), no prominent yield point is observed in EA-2 to EA-8 samples which implies the absence of any neck formation and strain hardening in these samples. In such cases, both the maximum strength and the breaking strength become equal which are the characteristics

Table 5 Thermal properties of ATAAO cured epoxy samples obtained from thermogravimetric analysis

Curing Temper	Luring Temperature											
363.15 K					393.15 K							
Sample Code	Curing Time (min)	T _{onset} (K)	T ₁₀ (K)	T _{max} (K)	T _g (K)	Sample Code	Curing Time (min)	T _{onset} (K)	T ₁₀ (K)	T _{max} (K)	T _g (K)	
EA-1	30	553.21	520.15	660.56	423.21	EA-5	30	573.21	605.15	663.15	431.74	
EA-2	60	558.49	604.15	662.26	426.90	EA-6	60	573.21	610.15	675.15	452.88	
EA-3	90	559.63	607.15	667.15	430.62	EA-7	90	580.32	620.15	664.15	456.37	
EA-4	120	573.14	620.15	664.15	435.20	EA-8	120	580.32	625.15	672.15	481.61	





Fig. 9 The Stress-strain curves of oligomer cured DGEBA epoxy samples at (a) 90 °C and (b) 120 °C curing temperatures



Table 6Tensile properties ofATAAO cured epoxy samples

Curing Temperature	Curing Time (min)	Sample Code	Young's Modulus (MPa)	Stress @ break (MPa)	Strain @ break (%)
363.15 K	30	EA-1	5.93 ± 0.16	7.79 ± 0.24	21.61 ± 0.27
	60	EA-2	15.01 ± 0.13	12.28 ± 0.22	1.62 ± 0.19
	90	EA-3	30.20 ± 0.06	3.10 ± 0.08	0.36 ± 0.08
	120	EA-4	34.31 ± 0.02	7.41 ± 0.08	0.23 ± 0.11
393.15 K	30	EA-5	10.15 ± 0.24	3.10 ± 0.26	0.31 ± 0.26
	60	EA-6	29.61 ± 0.25	7.38 ± 0.38	0.54 ± 0.52
	90	EA-7	38.41 ± 0.16	20.79 ± 0.38	0.54 ± 0.27
	120	EA-8	41.09 ± 0.20	31.92 ± 0.59	0.85 ± 0.41

of brittle materials. Table 6 displays the tensile properties such as Young's modulus, stress at break, and strain at break of the samples after curing at 363.15 K and 393.15 K for different curing durations.

Young's modulus, which describes the stiffness of the material, is increased from 5.93 MPa to 41.09 MPa for EA-1 to EA-8 samples, respectively. The greatest stress that a material can bear while stretching before rupturing or deforming is known as stress at break, which determines the material's ultimate tensile strength. A higher tensile strength (31.92 MPa) is observable for the sample cured at 393.15 K for 120 min as shown in Fig. 9b. This higher strength at higher curing conditions can be attributed to the maximum crosslinking to form a 3D network of epoxy cured at 393.15 K for 120 min. In addition, a greater extent of epoxy curing at 393.15 K can also be another reason to achieve higher tensile strength while facilitating earlier gelation [40, 41]. Another tensile parameter i.e. strain at break, which measures the percentage change in length of the sample

before fracture, describes the sample's elongation (%). This property was found to be decreased while increasing curing temperature and duration due to an extensive crosslinking generated in the samples. However, the EA-1 sample presented more elongation, which was cured at 363.15 K for 30 min, due to less possible crosslinking.

While comparing thermal and tensile properties, an increase in Young's modulus of the samples is observable with an increase in the T_g value of the samples as shown in Tables 5 and 6. This increase in both glass transition temperature and Young's modulus with curing temperature and duration is mainly attributed to the formation of a complex 3D network of epoxy with ATAAO with increasing curing conditions [36, 37]. As the curing temperature and time increased, the process of epoxy curing with ATAAO approached completion while restricting the motion of chains in 3D cross-linked rigid structure which eventually led to the higher stiffness and T_g of the sample cured at 393.15 K for 120 min as compared to sample cured at

Curing Agent	Curing Temperature and Dura- tion	Young's Modulus (MPa)	Stress @ break (MPa)	T _{onset} (K)	T _g (K)	Reference
Methyl tetrahydro phthalic anhydride (MTHPA)	393.15 K and 600 min	4140	NA	NA	401.62	[7]
Nadic anhydrie (NA)	393.15 K and 600 min	4870	NA	NA	427.48	
Amine terminated aliphatic amide oligomer prepared from PDA and IPC	393.15 K and 60 min	23.01	44.1	370	NA	[19]
Amine terminated aromatic amide oligomer prepared from ODA and IPC	393.15 K and 60 min	35.15	58.3	372	NA	
Diaminodiphenyl sulfone	453.15 K and 120 min	2680	87.2	NA	NA	[20]
Different amino Acids	393.15 K and 443.15 K, and 120 min	2600-3500	39.4–46.4	NA	371.25-461.45	[21]
Amine terminated aromatic amide oligomer prepared from PPDA and IPC	363.15 K and 393.15 K, and 30, 60, 90 and 120 min	5.93-41.09	7.79–31.92	553.21-672.15	423.21-481.61	This study

Table 7 The comparison of thermal and tensile properties of cured DGEBA epoxy obtained in the present study with previous studies



363.15 K for 30 min. Moreover, the formation of crosslinked epoxy networks with different amine-type curing agents such as aliphatic, cycloaliphatic, and aromatic amines at variable curing temperatures and time is also evident in many studies wherein the cured epoxy posed improved thermal and mechanical properties [42–45].

This investigation provides insight into the variation in the extent of curing, thermal, and tensile properties of the DGEBA epoxy cured with ATAAO by varying curing temperature and curing durations which were not studied before. Moreover, Table 7 presents the comparison of results obtained in this study with the previous studies.

Evaluation of Surface Morphology of Cured Epoxy Films

The microscopic images in Fig. 10 show a homogeneous structure without any phase separation of ATAAO-cured epoxy with slight bumps and small globular and low moisture content. Moreover, the relatively stiff and rougher surface of completely cured epoxy than the soft and smooth surface of partially cured epoxy (Fig. 10a & b) can be seen in the micrographs, which indicates how much curing temperature and time are essential in the curing of epoxy resins. The presence of a smooth surface of neat epoxy as compared

to the rough surface of cured epoxy was also noticed in two different studies [46–49].

Conclusions

A semi-crystalline amine-terminated aromatic amide oligomer was synthesized successfully and characterized by ¹HNMR, FT-IR, and XRD. The disappearance of peaks corresponding to terminal epoxy (d), terminal amine (bb), and amide (bb), and the appearance of multiple peaks at 3.69–4.65 ppm in ¹HNMR confirmed the curing of DGEBA epoxy. Moreover, the ring-opening epoxy curing phenomenon was also confirmed by the absence of terminal epoxy ring bands and the appearance of hydroxyl and some aliphatic bands in FT-IR spectra. The extent of epoxy curing was varied while changing the curing conditions and maximum epoxy curing (~100%) was achieved at a curing temperature of 393.15 K and 120 min curing time. The increase in T_{onset} (553.21 K to 580.32 K), T_g (423.21 K to 481.61 K), and Young's modulus (5.93 MPa to 41.09 MPa) was attributed to the increase in the extent of cross-linking with increasing curing temperature and time. Moreover, an amorphous and homogeneous structure of ATAAO cured epoxy with slight bumps, small globular, and without any phase separation was observed which further led to an excellent compatibility of epoxy resin for amine-terminated aromatic amide oligomer.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interest The authors declare no conflict of interest.

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