



Studies on glass reinforced laminates based on amide oligomers – epoxy resin based thermosetting resin blends

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Abstract: In many applications thermosets are the materials of choice for long-term use because they are insoluble and infusible high-density networks. Amide oligomers are synthesized in presence of urea, ethylene diamine and melamine with bisphenol A and benzene1,4 diol. Amide oligomers were characterized by number average molecular weight ($\overline{M}_n$), % nitrogen, % formaldehyde and IR spectral studies. Glass reinforced laminates of amino resin – epoxy resin were prepared and characterized by their synergetic thermal stability by thermo gravimetric analysis (TGA), mechanical properties, chemical resistance and fibre content.

Key Words: laminates, oligomer, thermosets etc.

I. Introduction

Over a past few decades composites, plastics, ceramics have been the dominant engineering materials. The areas of applications of composite materials have grown rapidly and have even found new markets. Modern day composite materials consist of many materials in day to day use and also being used in sophisticated applications while composites have already proven their worth as weight saving materials the current challenge is to make them durable in tough conditions to replace other materials and also to make them cost effective. This has resulted in development of many new techniques currently being used in the industry. New polymer resin matrix materials and high performance fibres of glass, carbon and aramid which have been introduced recently have resulted in steady expansion in uses and volume of composites. This increase has resulted in obvious reduction of cost. High performance FRP are also found in many diverse applications such as composite armoring design to resist the impact of explosions, wind mill blades, industrial shafts, and fuel cylinders for natural gas vehicles paper making rollers and even support beams of bridges. Existing structures that have to be retrofitted to make them seismic resistant or to repair damage caused by seismic activity are also done with help of composite materials. Development of advanced composite materials having superior mechanical properties opened new horizons in the engineering field. Advantages such as corrosion resistance, electrical insulation, reduction in tooling and assembly costs, low thermal expansion, higher stiffness and strength, fatigue resistance, such as greater stiffness at lower weight than metals, etc., have made polymer composites widely acceptable in structural applications. However, the disadvantages of composite materials cannot be ignored: their complex nature, designers' lack of experience, little knowledge of material databases and difficulty in manufacturing are barriers to large-scale use of composites.

Various experimental approaches have been developed to investigate these properties. Liang et al. [1] studied the interfacial properties and its impact on tensile strength in unidirectional. Sreekala et al. [2] found the significant decrease in the flexural strength was observed at the highest EFB fibre volume fraction of 100% which was due to the increased fibre – to – fibre interactions and dispersion problem which results in low mechanical properties of composite. Yamamoto et al. [3] reported that the structure and shape of silica particles have significant effects on the mechanical properties such as fatigue resistance, tensile and fracture properties. Singha et al. [4] reported a study on the synthesis and mechanical properties of new series of green composites involving Hibiscus Sabdariffa fibre as a reinforcing material in urea – formaldehyde (UF) resin based polymer matrix. Mahapatra et al. [5] described the development of multi-phase hybrid composites consisting of polyester reinforced with E-glass fibre and ceramic particulates. Aruniit et al. [6] studied to find out how the filler percentage in the composite influences the mechanical properties of the material. Ibrahim [7] investigated the effects of reinforcing polymer with glass and graphite particles on enhancing their flexural properties. In thermosetting polymers, the liquid resin is converted into a hard rigid solid by chemical cross-linking which leads to the formation of a tightly bound, three dimensional network. The mechanical properties depend on the molecular units making up the network and between cross-links and the length density of cross-links. [8-10] There are different types of amine curing agents (1) aliphatic like Triethelentetramine (TETA), (2)

cycloaliphatic, (3) aromatic like (DDM), (4) polyamine adduct, etc. Numerous grades of epoxy resins and curing agents are formulated for a wide variety of applications. [11]

The objective of this work is to investigate the effect of amide oligomer – epoxy blended composite reinforced with glass fibre.

II. Experimental

A. Materials

All the chemicals used were of laboratory grade. E-type of glass woven fabric 0.25 mm thick was used for laminate fabrication. Commercial epoxy resin, DGEBA (Diglycidyl ether of bisphenol A) was obtained from Synpol, Ahmedabad, Gujarat, India. It had an epoxy equivalent 200, estimated by standard method [12].

B. Synthesis of amide oligomers

Dimethylol urea and trimethylol urea were synthesized according to standard method reported in literature. [13]

C. Syntheses of resin based on dimethylol urea+Bisphenol A (UBA)

Take the dimethylol urea (120gm) Bisphenol A (228gm) and THF (60ml) as a solvent in three neck flask. All these ingredients are mixed thoroughly at 60°C and then add concentrated HCl as a catalyst. Now raise the temperature at 80-85 °C for 7 hours. After the preparation of resin mixture was allowed to cool.

D. Syntheses of resin based on ethylene diamine+Bisphenol A (EBA)

Take ethylene diamine (120gm) and (200ml) Toluene as a solvent and (162gm) Formalin and (2ml) HCl as a catalyst, all these ingredients take in three neck flask. Then after some heating period at 50 to 60 °C and then add 228 gm Bisphenol A and stirred for 2-3 hours at 90°C and resin are prepared. In this process dean and stark condenser is used because Toluene is removed from this system due to heating and take it in small beaker.

E. Syntheses of resins based on trimethylol melamine+Bisphenol A (MBA)

First take melamine trimethylol (TMM) (252gm) and (70ml) water as a solvent and Bisphenol A (114gm) in a three neck flask. After mixing of these ingredients add aqua.KOH as a catalyst and raise the temperature 60 to 90°C and after 2 to 3 hours resin is prepared.

F. Syntheses resin based on dimethylol urea + Benzene 1,4diol (UB)

Take dimethylol urea (120gm) and THF (tetra hydro furan) (60ml) as a solvent and after this add (228gm) benzene1,4diol take this all reactants in three neck flasks and add conc. HCl as a catalyst and reflux at 60°C and raise the temperature at 80 to 95 °C to 3 to 4 hours. After the preparation of resin mixture was allowed to cool.

G. Syntheses resin based on ethylene diamine+Benzene 1,4diol (EB)

Take Ethylene diamine(120gm) and Toluene (200ml) as a solvent and Formalin (160gm) and mixed these ingredients in three neck flask and then Benzene1,4diol (110gm) and conc. HCl(2ml) as a catalyst add in three neck flask. In this process dean and stark condenser is used because Toluene is removed from this system due to heating and take it in small beaker. In this process raise the temperature 60 to 100°C for three hours.

H. Syntheses resin based on trimethylol melamine +Benzene 1,4diol (MB)

Take Melamine Trimethylol (252gm) and add water (70ml) as a solvent in three neck flask and then add Benzene1,4diol (110gm) and then mixed these ingredients in three neck flask and add aqua.KOH as a catalyst in three flask and raise the temperature at 60 to 90°C for 3 to 4 hours and then resin is prepared.

III. Characterization

FTIR spectra of all the amide oligomers were recorded using Perkin Elmer Lambda-19 FTIR spectrometer employing a thin layer of the sample on a KBr cell. Number average molecular weight of the amide oligomer were measured by using vapour pressure osmometer Knaller (Germany K.7000) using DMF as solvent as per ASTM D 3592-77. Corresponding % nitrogen by kjeldahl method and % formaldehyde of the amide oligomers were determined by standard method reported in literature [12,14]. The viscosity of amide oligomers were measured by Brookfield RVF viscometer as per ASTM D 1824.

IV. Laminates Fabrication

Glass reinforced laminate were prepared employing hand layup prepreg formation technique. The composites were fabricated using resin to glass fabric ratio of 60:40. The resin was prepared and stirred for 5- 10 minutes and the resultant mixture was applied on a glass fabric (15 X 12) with the brush and allowed to dry. Ten such dried prepregs prepared in similar way were stacked one over other and pressed between two steel plates using teflon sheet as mould releasing agent. Subsequently, these plates were pre-cured in a compression moulding machine at 65-70°C for 10 minutes. The pre-curing temperature was raised to 150°C and 150-200 psi pressure was applied for 15-20 minutes. After completion of curing the plates were cooled to 50°C before pressure was released. These composites were tested as per various standard methods [15]. Specimens of dimension 130 mm X 12.7 mm were taken for measurement of flexural strength as per ASTM D 790, employing Instron testing machine. The tests were carried out at a crosshead speed of 100 mm/min and span length of 70 mm respectively. Izod impact strength of un-notched samples of dimensions 70 mm X 13 mm was measured as per ASTM D 256.

Rockwell hardness of the laminates was measured employing specimens of dimensions 25 mm X 25 mm as per ASTM D 785. All the mechanical tests were conducted at room temperature. Chemical resistance tests were carried out as per ASTM D 543. Test specimens of dimensions 76.2 mm X 25.4 mm were tested in presence of 10 % NaOH, 10 % H₂SO₄, Dioxane, DMF and water. Thermal stability of all glass reinforced laminates was carried by thermo gravimetric analyzer (TGA) on a Dupont 950 thermo gravimetric analyzer at a heating rate of 10°C / min in air atmosphere. The weight loss at different temperatures was recorded in the temperature range of 40-600°C.

V. Results & Discussion

Amide oligomers are obtained by polycondensation reaction and characterized them by different ways. % nitrogen of all the amide oligomers was characterized by kjeldahl method. Number average molecular weights ($\overline{M}_n$) for all the amide oligomers were observed in the range of 3000 – 3500 gm / mole. The viscosity data of amide oligomers were found in the range of 180-380 cP. The results are shown in Table 1.

FTIR spectra of the amide oligomers were revealed the following results. A strong and sharp band at 1510 cm⁻¹ due to characteristic of p-substituted derivative of bisphenol A was observed. The other strong band around 1380 cm⁻¹ is probably assigned to methyl group of bisphenol A. Similarly, a strong C-O-C stretching band with its maximum in the range between 1255-1245 cm⁻¹ is due to the presence of aromatic aliphatic ether. Two distinct vibrational frequencies at 2945 and 2880 cm⁻¹ indicates characteristics of aliphatic C-H stretching vibration of bridged methylene groups of amide oligomers. Absorption bands corresponding to aromatic ring hydrogen out of plane stretching vibration for 1, 4 substituted were characterized by a band at about 833 cm⁻¹. The other band in the range of 1625-1440 cm⁻¹ due to C=C stretching is observed this is due to mono substituted benzene and its derivatives. In the range of 1150 – 1060 cm⁻¹ is C-O stretch CH₂-O-CH₂ band is present due to ethers. In range of 1720 -1700 cm⁻¹ stretch band due to ketones C=O band is observed. A characteristic strong band at 1720-1727 cm⁻¹ in all amide oligomers indicates good agreement with data reported in literature for different class of amide oligomers [16].

The mechanical properties of glass reinforced laminates based on amide oligomers – epoxy resin prepared is represented in Table 3. The data of flexural and impact strength values of glass reinforced laminates based on amide oligomers – epoxy showed synergistic effects. This behavior can be explained on the basis of permanent physical chain entanglements resulting due to the presence of aromatic moiety of bisphenol A and 1,4 benzene diol. [17]. Rockwell hardness of all glass reinforced laminates samples were found in the range of 85 to 100 in .R. scale at 23°C and 50% RH.

Thermal stability of all amide oligomers – epoxy resin based glass reinforced laminates were carried by TGA on a Dupont 950 thermo gravimetric analyzer at a heating rate of 10°C / min in air atmosphere. In order to determine the thermal stability percentage (%) weight loss at different temperature were calculated and the data of thermo gravimetric analysis are shown in Table 2. Thermo gravimetric analysis chart of all amide oligomers – epoxy resin based glass reinforced laminates are shown in Figure 1&2. The observation of thermo grams of all laminates revealed following conclusion. In all composites about 4 to 6 % weight loss was observed up to 200°C and about 15 to 25% weight loss was observe up to 350°C temp. After this temperature range very slow rapid loss was observed around 400°C temperature furthermore the thermo grams of all composites reveals that about 50% of weight loss occurred in the temperature range of 400-450°C temperature. Thermo gravimetric studies indicates the good interpenetration of thermosetting epoxy resin composites and these composite have very good thermal stability which proves suitability for high performance applications.

There are different methods for the determination of fiber content of glass reinforced composite. In acid dissolution method a specific dimension of composites is dissolve in strong H₂SO₄ and the results obtained is good agreement with the ratio of matrix: reinforcement. The results of chemical resistance (ASTM D 543) to various reagents are represented in Table 4. Examination of these data indicated that each of the amide oligomers – epoxy resin based glass reinforced laminates were mostly stable in 1,4-dioxane, DMF and distilled water. However, very little loss in glass and negligible changes in weight and thickness were observed in standard sodium hydroxide solution.

VI. Conclusion

Synergistic effects observed in mechanical properties exhibited by all amide oligomer – epoxy resin based glass reinforced laminates confirmed that interpenetration has occurred in amide oligomer – epoxy resin. The laminates exhibited higher flexural, impact strength, chemical resistance of the individual network component increased in the glass reinforced laminates of amide oligomer – epoxy resin. Thus, amide oligomer – epoxy resin reinforced with glass fibers can be utilized commercially as an excellent polymer matrix for engineering applications.

VII. References

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Table 1: Characterization of amide oligomers

Sr. No.	Resin system	% Nitrogen	% Free formaldehyde	Number average molecular weight (M_n)
1	UBA	3.717	13.5	3420
2	EBA	14.868	15.41	2980
3	MBA	1.386	17.17	3527
4	UB	5.355	13.00	3380
5	EB	6.993	15.16	3000
6	MB	3.213	17.18	3480

Table 2: Thermo gravimetric analysis (TGA) of laminates based on amide oligomer – epoxy resin system

Sr. No.	Laminates Resin System (Amide Oligomer – Epoxy Resin)	Color	% weight loss at different temperature ($^{\circ}$ C)										
			100	150	200	250	300	350	400	450	500	550	600
1.	UBA – Epoxy resin	Light yellow	0.725	2.899	4.349	6.523	10.146	18.842	28.988	31.887	34.05	35.502	38.487
2.	EBA – Epoxy resin	Yellow	1.5	2.99	5.23	11.2	29.11	44.63	50	51.5	53.74	55.92	58.27
3.	MBA – Epoxy resin	Light yellow	0.73	1.46	2.9	5.74	9.43	15.22	18.85	23.92	31.16	37.69	41.31
4.	UB – Epoxy resin	Brown	1.48	2.95	6.62	10.3	17.65	25.00	41.91	53.68	56.62	61.03	65.45
5.	EB – Epoxy resin	Brown	1.48	2.95	6.62	10.3	17.65	25.0	41.91	53.68	56.62	61.03	65.45
6.	MB – Epoxy resin	Brown	0.75	1.49	2.23	3.71	7.42	12.6	18.52	43.71	45.19	46.67	48.15

Figure 1: Thermo gravimetric analyses of amide oligomer – epoxy resin glass reinforced laminates

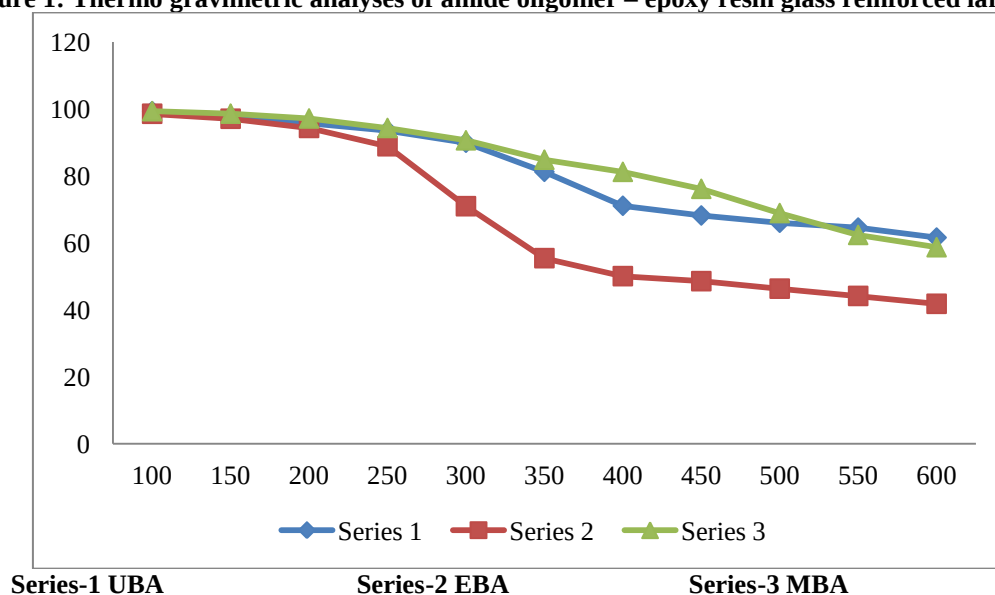


Figure 2: Thermo gravimetric analyses of amide oligomer – epoxy resin glass reinforced laminates

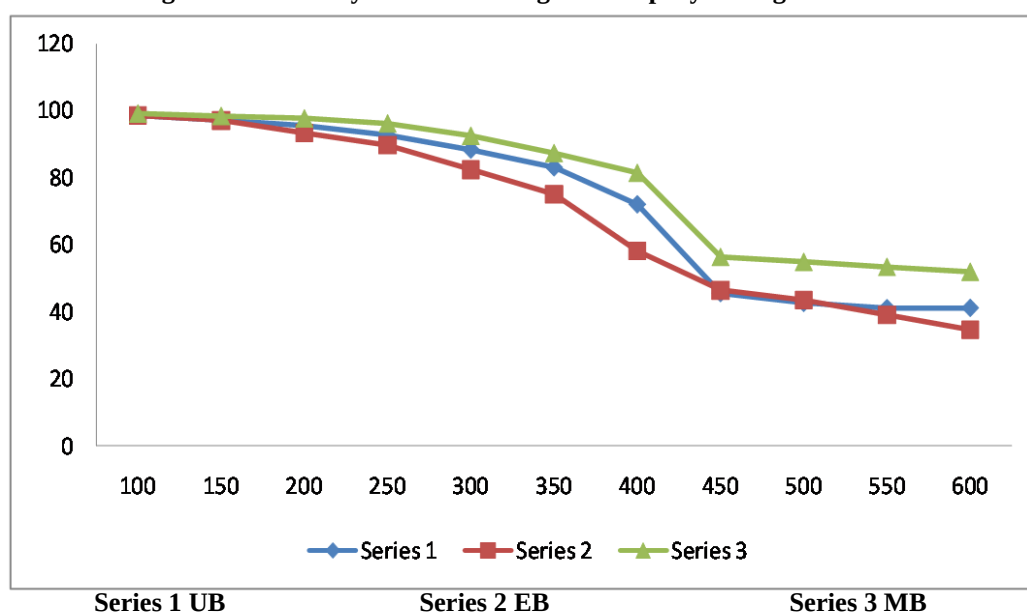


Table 3: Mechanical Properties of amide oligomer – epoxy resin glass reinforced laminates

Sr. No.	Laminates Resin System (Amide Oligomer – Epoxy Resin)	Impact Strength (J/cm.)	Flexural Strength (KgF/cm.)	Rockwell Hardness (R Scale)
1.	UBA – Epoxy resin	400	430	85
2.	EBA – Epoxy resin	350	500	90
3.	MBA – Epoxy resin	410	550	95
4.	UB – Epoxy resin	450	600	100
5.	EB – Epoxy resin	500	640	90
6.	MB – Epoxy resin	480	620	90

Table 4: Chemical resistance & Fibre Content of glass reinforced laminates of amide oligomer – epoxy resin to standard reagents

Sr. No.	Laminates Resin System (Amide Oligomer – Epoxy Resin)	10% NaOH Solution		10% H ₂ SO ₄ Solution		1,4 Dioxane		DMF		Water	
		% Change in Weight	% Change in thickness	% Change in Weight	% Change in thickness	% Change in Weight	% Change in thickness	% Change in Weight	% Change in thickness	% Change in Weight	% Change in thickness
1.	UBA – Epoxy resin	1.84	1.02	0.84	0.60	NC	NC	NC	NC	NC	NC
2.	EBA – Epoxy resin	1.85	0.72	0.80	0.65	NC	NC	NC	NC	NC	NC
3.	MBA – Epoxy resin	1.75	1.05	0.85	0.55	NC	NC	NC	NC	NC	NC
4.	UB – Epoxy resin	1.70	0.85	0.75	0.75	NC	NC	NC	NC	NC	NC
5.	EB – Epoxy resin	1.80	0.99	0.84	0.90	NC	NC	NC	NC	NC	NC
6.	MB – Epoxy resin	1.82	1.00	0.84	0.90	NC	NC	NC	NC	NC	NC