Acrylonitrile–Triethylene Tetramine Adduct Hardener Systems for Epoxy Resin

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Synopsis

Triethylene tetramine (TETA) has been chemically modified to different extents using acrylonitrile (AN) as chain extender for the hardener system of epoxy resin. The modified hardeners have been characterized and used to make epoxy casting and glass reinforced composites. The neat epoxy matrices have been evaluated in terms of mechanical and thermal properties, while their glass fibre reinforced composites have been characterized mechanically. It has been observed with neat resin casting that the Izod impact strength increased from 14.89 to 67.17 kJ/m^2, but the Rockwell hardness and glass transition temperature decreased from 83.1 to 30.8 and 146.2 to 59.7°C, respectively, as the extent of modification of TETA increased through the utilization of 0 to 3 mol AN for epoxy curing. Hardener based on adduct of 1 mol TETA and 3 mol AN was found most suitable for making epoxy prepreg with 1 month shelf life at −5°C.

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers. They are widely used for many important applications such as coatings, adhesives, and matrix resin for advanced composite materials.[1-4] The application characteristics of the epoxy systems has been limited, because of their brittleness. Many attempts have been made to improve the impact energies of the network, while at the same time retaining the other properties.[5-9]

Aliphatic polyamine epoxy hardener systems generally have short gel time of about 15–60 min. Therefore, it is difficult to handle bulk quantities of resin mix for the fabrication of thick laminates. Chain extension of the amines may be one of the ways to reduce brittleness of the resin as well as increase its gel time. Among this category falls acrylonitrile (AN), which reacts with compounds containing labile hydrogen atom to form β–substituted propionitriles.[9-15] Such β–substituted products or their modified products are widely used to produce plasticizers, emulsifiers, floatation reagents, dyes, fungicides, and lubricant additives.[15-22] But so far, the suitability of AN modified TETA as hardener for epoxy resin has not been critically studied.

The object of this investigation is to prepare hardener by reacting AN with TETA and to utilize the modified hardener with a view to improve the gel time of epoxy curing system and to reduce the brittleness of the cured product. The hardener system has also been examined for its suitability as a curing agent for making epoxy prepregs.

EXPERIMENTAL

Materials Used

(i) Acrylonitrile (AN), BDH was freed from inhibitors by extracting it out by 4% sodium hydroxide solution. The inhibitor free AN was distilled under reduced pressure and the distillate was used to carry out reactions with the tetramine.

(ii) Triethylene tetramine (TETA), product of GS chemicals, New Delhi, was distilled under reduced pressure before use in all experiments.

(iii) Epoxy resin of diglycidyl either of bisphenol-A (DGEBA), a Ciba-Geigy product (LY 556) was used to prepare castings and composites.

(iv) Plain weave glass fabric received from Swan Corporation, Ahmedabad, was used to fabricate composites.

Preparation of Adduct of TETA and AN

Four adducts of TETA were prepared by reacting it with 1, 2, 3, and 4 mol AN; the adducts were designated 11TAN, 12TAN, 13TAN, and 14TAN, respectively. The rate of addition of AN was maintained in such a way that the temperature of the overall mixture always remained within the range of 40–42°C. For this purpose, vigorous agitation and rate of addition of AN as 3.5 mL/min to 450 mL of TETA placed in cold water bath was adequate; e.g. 202.9 mL of AN added to 450 mL of TETA for the preparation of 11TAN. After the addition of AN was finished, the mixture was allowed to age until the viscosity of the system became stationary. The end products were characterized by IR and NMR spectroscopies.

Measurement of Gel Time and Peak Exotherm

For the determination of these properties, 100 g epoxy resin was mixed thoroughly with stoichiometric proportion of each hardener separately. The resin mix was attached with the probe of the data logger instrument (Model CDL 101) from Century Instruments, Ltd., Chandigarh. The temperature of the reaction mix increased with time as the curing reaction progressed. The plot of time against temperature was obtained with the recorder. The gel time was calculated from the cusp (intersection of the curves) in the first transition while the system became rubbery, indicating the start of gellation (typical plot shown in Fig. 1); the corresponding peak exotherm was noted from the graph.

Preparation of Casting

Castings were prepared by pouring the mixture of stoichiometric proportion of epoxy resin and different hardeners into the mold space (25 × 20 × 0.4 cm) enclosed between two polished (silicone resin coated) parallel steel plates. The curing was done at room temperature (32°C) for 24 h followed by post-curing at 120°C for 2 h in each case.

Preparation of Prepregs

They were prepared by brushing resin mix over oven dried fabric and were sealed in polyethylene bag and preserved at −5°C in a refrigerator. The pre-
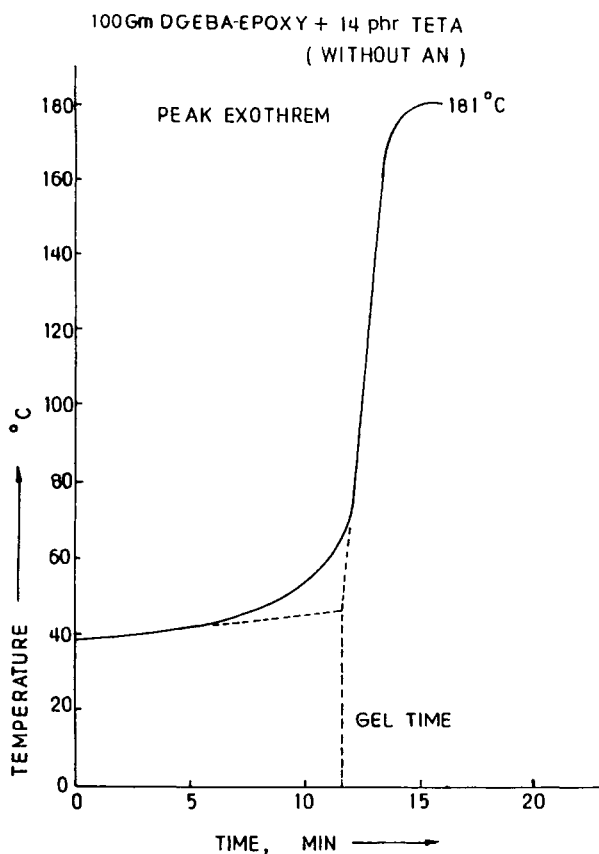
Fig. 1.   Curing curve for DGEBA/TETA resin system.

served prepregs were thawed to room temperature and then stacked for lamination as and when required.

Fabrication of Laminates

Laminates were prepared by applying resin mix over dried glass fabric and which was then cured at 120°C for 3 h under a pressure of 50 kg/cm^2 in a compression molding press. Two types of composites—one about 4 mm thick and the other about 8 mm thick—were fabricated. The ca. 4 mm thick laminates were used for measuring the tensile and flexural properties, while ca. 8 mm thick laminates were used for the measurement of impact and interlaminar shear strength (ILSS) properties.

Swelling Measurement

Percent volume swelling was determined by measuring the densities of the neat casting (or composite) and the swollen casting (or composite) after having undergone swelling in acetone for 24 h at 40°C.

Mechanical Property Measurement

The flexural, tensile, impact, and interlaminar shear strength properties were determined according to the desired specification of ASTM, such as D 790-81, D 3039-76, D 256-81, and D 2344-84, respectively.

Thermal Analysis

For thermogravimetric analysis (TGA), Du Pont 1090 thermal analyzer with a TGA module was used to evaluate the thermal behavior of the cured resins. The measurements were done in nitrogen atmosphere (flow rate 50 ml/min) at a heating rate of 10°C/min. The initial decomposition temperature (T_i) and final decomposition temperature (T_f) were obtained by extrapolation. The temperature of maximum rate of weight loss (T_m) and char yield (Y_c) at 550°C were also obtained from thermogravimetric traces (Fig. 2).

Dynamic Mechanical Analysis (DMA)

DMA technique with the a Du Pont 982, dynamic mechanical analyzer was used to determine the important parameters such as out-of-phase loss elastic modulus (E''), in-phase storage elastic modulus (E') and their ratio, i.e., elastic damping factor (tan δ) at different temperatures at a fixed frequency. The transition temperature were determined from the thermomechanical profiles. The operating condition for DMA was as follows. Method: resonant; size: 19.2 $\times$ 12 $\times$ 4.5 mm; rate of heating 5°C/min, oscillation amplitude: 0.5 mm peak to peak; clamping distance: 8.0 mm; moment of intertia: 2.5 gm^2.
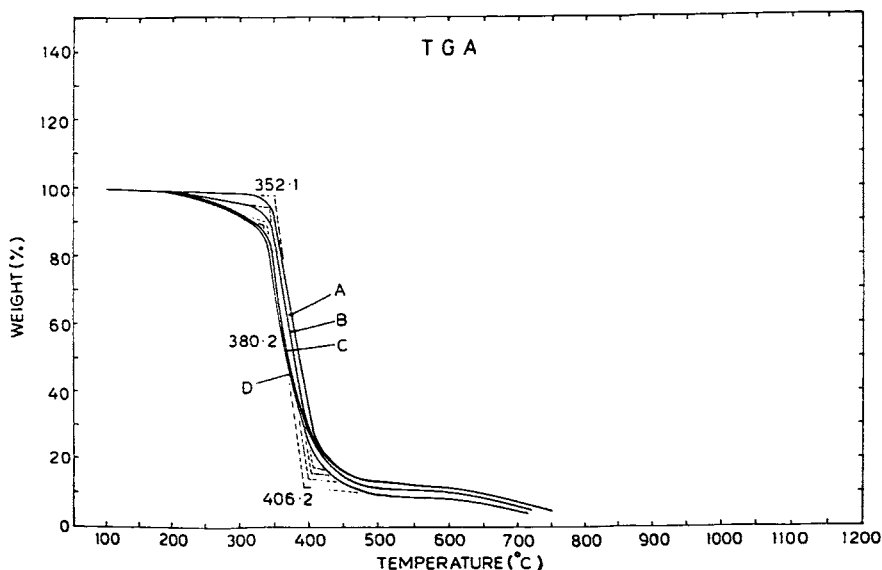

Fig. 2. Thermogravimetric traces of different epoxy matrices cured by TETA and modified TETA as hardener: (A) DGEBA/TETA system; (B) DGEBA/11TAN system; (C) DGEBA/12TAN system; (D) DGEBA/13TAN system.

Thermo-mechanical Analysis (TMA)

TMA for determination of transition temperature was performed with a Du Pont 943 instrument, employing a load of 5 g through a probe of size 4.3 mm, while the rate of heating was maintained at 5°C/min.

RESULTS AND DISCUSSION

AN reacts with TETA exothermally, and the resulting adducts are transparent liquids with higher viscosities than either of TETA or AN. The increase in viscosity is due to the extension of chain length in the amine and is also a measure of progress of reaction between TETA and AN. The viscosity of each system gets stabilized at different time intervals. The overall properties of the adducts are shown in Table II.

The IR study indicated absorption near 2260 cm^{-1} thereby showing the presence of nitrile group ($-C\equiv N$) in all the adduct systems. The number of methylene groups in the adduct should increase with the incorporation of AN into TETA. The ^{1}H-NMR analysis of TETA and the adducts shows the presence of number of methylene hydrogen atoms in TETA, 11TAN, 12TAN, 13TAN, and 14TAN as 12, 16, 20, 24, and 28, while that for amine hydrogen atoms as 6, 5, 4, 3, and 2, respectively. Thus the NMR spectra are consistent with the structure having desired number of hydrogen atoms attached to nitrogen atom. Therefore, the reaction between AN and TETA may be schematically presented as

$$H_2NCH_2CH_2NH\wedge NH_2 + CH_2=CHCN \rightarrow H_2NCH_2CH_2NH\wedge NHCH_2CHCN$$

Gel Time, Peak Exotherm

It has been observed that with the chemical incorporation of AN into TETA, the gel time increased, while peak exotherm decreased gradually for the systems with TETA to 14TAN when used as hardener of DGEBA epoxy resin (Table I). The gel time with the TETA/epoxy system is minimum, while it is maximum with the 14TAN/epoxy system. The reduced functionality of the modified

TABLE I
Properties of AN–Modified–TETA Hardener Systems

Hardener	Density (g/cc)	Kinematic viscosity at 40°C (cS)	Boiling point (°C)	Gel time for reaction with 100 g epoxy resin (min)	Peak exotherm for reaction with 100 g epoxy resin (°C)
TETA	0.9792	17.3	285	11.6	181.0
11TAN	1.0217	44.5	330	21.0	176.0
12TAN	1.0315	153	385	40.0	103.2
13TAN	1.0513	464	> 400	[a]	46.3
14TAN	1.0632	628	> 400	[a]	40.2

[a] Mix remained soft even after 24 h.

TABLE II
Properties of DGEBA–Epoxy Castings

Hardener	Density of casting (gm/c.c.)	% Volume swelling	Impact strength (Izod) (kJ/m^2)	Rockwell hardness	Tan δ	Flexural strength (MPa)[a]	Flexural modulus (GPa)[a]	Tensile strength (MPa)[a]
TETA	1.2032	0.89	14.89	83.1	0.490	98.6	2.22	55.24
11TAN	1.1988	0.95	25.12	70.7	0.675	101.4	2.33	58.99
12TAN	1.1977	3.97	56.73	48.6	0.925	106.2	2.40	65.20
13TAN	1.1916	13.62	67.17	30.8	1.210	99.8	2.36	65.00

[a] $1GPa = 10^3 MPa = 10.2 \times 10^3 kg/cm^2$.

hardener results in lower crosslink density, lower peak exotherm, and improved gel time.

Casting

The casting obtained with the use of 14TAN was too flexible and soft, as the level of chain extension in the adduct was more than desired. Therefore, 14TAN was not used for further experimentation.

It was observed that the density of TETA cured resin was highest; therefrom the density decreased gradually and reached a lowest value of 1.1916 g/cc. associated with 13TAN cured resin (Table II). The chains are arranged most tightly in the epoxy/TETA matrix system; therefore the density of epoxy/TETA system is maximum.

Epoxy resin cured with TETA has the lowest swelling, while for that cured with 13TAN hardener the swelling is maximum; there is a gradual increase in volume swelling from TETA to 13TAN cured product (Table II). Due to the increase in the chain length of the polyamine molecule, the crosslink density in the epoxy matrix decreases, and the matrix becomes chemically plasticized sufficiently which results a matrix prone to swelling.

The Izod impact strength increased gradually from 14.89 to 67.17 kJ/m^2, while the Rockwell hardness decreased from 83.1 to 30.8 for the epoxy casting hardened by TETA as such to 13TAN (Table II). The impact strength value for the epoxy matrix associated with the use of TETA only is in good agreement with the reported impact strength for epoxy/ethylene polyamine matrix system.[23] The improvement of impact strength (apparently indicating reduction

TABLE III
Results of Thermogravimetric Analysis for the Neat Cured Resin

Hardener	T_i(°C)	T_f(°C)	T_m(°C)	Char yield (Y_c) at 555°C
TETA	352	406.2	380.2	12.5
11TAN	345	405.7	372.8	12.1
12TAN	343.5	399.0	366.0	10.8
13TAN	334	397.4	364.6	8.9

in brittleness) at the cost of hardness is attributed to the increased ductility in the matrix due to increased flexibility brought about by the increase in chain length and/or lower branching in the hardener system on modification.

The thermal stabilities of different matrices cured with the modified hardeners were evaluated by thermogravimetric analysis. The relative thermal stabilities of the matrices were assessed by comparison with the initial decomposition temperature (T_i). The TGA results are summarized in Table III. Initial loss in weight was observed in the range of 397–407°C in all matrix systems. The char yield (Y_c) at 550°C decreases slightly from TETA to 13TAN cured matrices. The T_i, T_f (final decomposition temperature), and T_m (temperature of maximum rate of weight loss) values decreased slightly with the increase of AN moiety in the matrix system through the hardeners. Thus no significant decrease in the thermal stability was observed.

Table IV reveals that the tensile strength, flexural strength, and flexural modulus of the epoxy resin cured with different TETA modified hardeners have not deteriorated; instead there is a marginal improvement in these properties. This improvement in the tensile and flexural properties is probably due to the lowering of peak exotherm and improvement of gel time for the systems with modified hardener. Slow curing at lower temperature allows the mix to set in without deterioration of such properties from thermal degradation.[24] Prolonged gel time also allows the system to solidify uniformly and prevents the system from stress concentration in the matrix.[25-27] The mechanical properties evaluated at room temperature could not be directly correlated to the glass transition temperature. This is not unusual, because the glassy state properties should be more closely related to the cohesive energy density than to the network structure.[28] Further, mechanical properties are expected to be dominated by such minor regions as microdefects in the resin.[28] The matrix should have an optimum crosslink density for better strength property.[29] Matrix with 13TAN system starts showing decrease in the properties due to lowering of crosslink density, however Table IV shows that there is no appreciable change in tensile and flexural properties.

$T_{E'}$ $T_{E''}$ and T_δ are the transition temperatures at which storage modulus,

TABLE IV
Properties of Glass Fabric Laminates Based on DGEBA–Epoxy Resin Cured
by Different Hardener Systems

Hardener	% Volume swelling	Impact strength (Charpy) (kJ/m^2)	ILSS (MPa)[a]	Tensile strength (MPa)[a]	Flexural strength (MPa)[a]	Flexural modulus (GPa)[a]
TETA	0.14	484.70	39.62	466.0	327.8	39.2
11TAN	0.39	566.93	38.99	466.4	336.4	—
12TAN	2.39	620.79	36.21	468.2	341.3	39.8
13TAN	4.68	648.92	35.8	456.5	340.1	38.44

[a] 1GPa = 10^3 MPa = 10.2×10^3 kg/cm^2.

loss modulus, and damping factor (tan δ), respectively, are maximum (Fig. 3). At $T_{E'}$ the storage modulus (E') starts decreasing abruptly from its maximum value. $T_{E'}$, $T_{E''}$, and T_δ are shown in Figure 3. $T_{E''}$ is the glass transition temperature (T_g), and it is obtained in our experiment for epoxy/TETA system as 146.2°C, which is close to the reported value for some epoxy/polyamine systems.[23] All these transition temperatures decreased as the extent of incorporation of AN into TETA for curing epoxy resin increased. Such a decrease in transition temperature may be attributed to the decrease in crosslink density in the epoxy matrix. The transition temperature obtained from TMA as shown in Figure 4 is in close proximity to T obtained from DMA (Fig. 3). The trend in decrease of these temperatures as reflected from TMA is similar to that obtained from DMA.

The tan δ_{max} is the value of tan δ at T_g which increased with decrease in glass transition temperature. The increase in ductility as reflected from hardness and impact values (Table II) causes the ratio of loss elastic modulus to storage elastic modulus to increase. The tan δ values for the systems clearly indicate the increase of viscous character in the casting with the incorporation of AN moiety in the matrix system. The main-chain motions may significantly influence the impact strength.[30] The trend of the tan δ value for the systems suggests that the increase in impact property for castings is due to the increase in the ability of the system to dissipate more vibrational energy as heat, rather than transmit it, owing to internal mobility of molecular chains in the polymer matrix.[31,32]
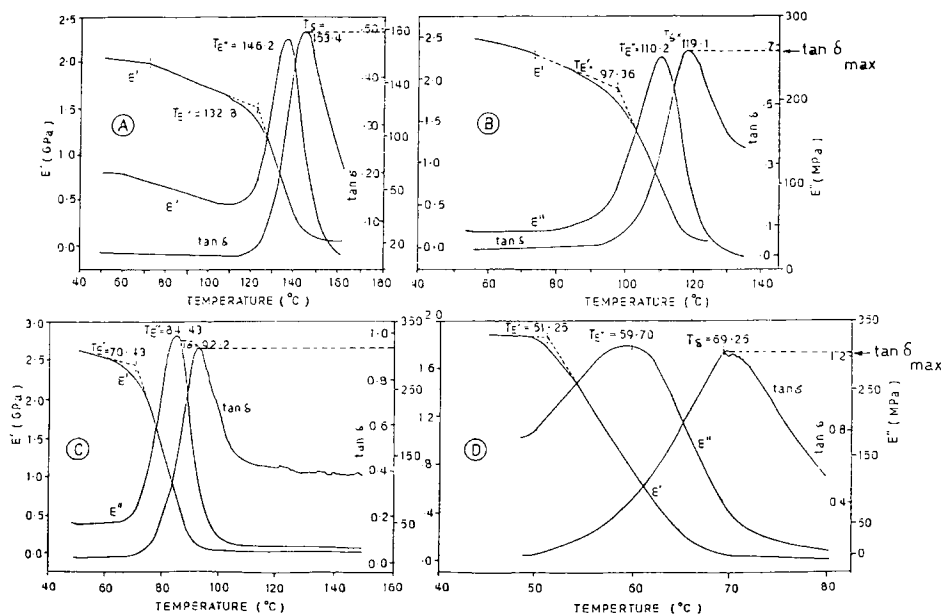

Fig. 3. Dynamic mechanical spectrum of different epoxy matrices cured by TETA and modified TETA as hardener: (A) DGEBA/TETA system; (B) DGEBA/11TAN system; (C) DGEBA/12TAN system; (D) DGEBA/13TAN system.
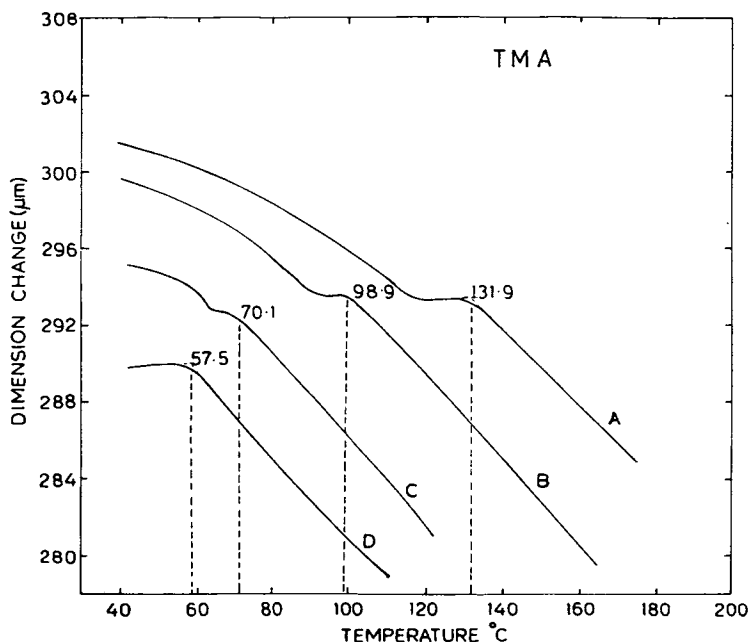
Fig. 4. Thermomechanical traces of different epoxy matrices cured by TETA and modified TETA as hardener: (A) DGEBA/TETA system; (B) DGEBA/11TAN system; (C) DGEBA/12TAN system; (D) DGEBA/13TAN system.

Laminate

It has been observed that the percent volume swellings for the composite laminates are in tune with the counterparts of the neat resin casting (Table IV).

Table IV shows that the impact strength of the composite increased from 484.70 to 648.92 kJ/m^2, while interlaminar shear strength (ILSS) decreased from 39.62 to 35.80 MPa, as the hardener system in the matrix shifts from TETA to 13TAN. The trend of the impact property for the composite is in tune with that of the corresponding neat resin casting. The impact strength of the composite increases at the cost of ILSS. The decrease in ILSS might have allowed the composite to dissipate more impact energy by debonding of fibers, thereby increasing the impact strength.[33-36] Table IV also reveals that the tensile and flexural properties of the composites are not much influenced by the change of hardener system.

One important advantage of DGEBA-epoxy/13TAN hardener system is that it provides a long gel time, and its neat casting shows good mechanical properties. With these observations it, was felt 13TAN hardener system would be suitable for making epoxy-prepregs using glass fabric as reinforcement for fabrication of laminate. It was observed that the mechanical properties such as flexural strength, flexural modulus, tensile strength, and tensile modulus were decreased by 5.3%, 17%, 7.6%, and 15%, respectively, when the laminates were fabricated from the prepreg after a month's storage at −5°C (Table V).

TABLE V

Results of Mechanical Properties of Glass Fabric Laminates Prepared from Prepreg
Based on DGEBA–Epoxy/13TAN Resin System[a]

Day of fabrication of laminates	Flexural strength (MPa)[b]	Flexural modulus (GPa)[b]	Tensile strength (MPa)[b]	Tensile modulus (GPa)[b]
0 th	314.3	39.4	346.6	34.9
15 th	305.3	38.8	345.1	32.8
30 th	297.7	32.6	320.2	29.7

[a] Curing temperature: 120°C; curing time: 3 h.
[b] $GPa = 10^3 MPa = 10.2 \times 10^3 kg/cm^2$.

CONCLUSION

There is a significant improvement in the gel time and reduction in peak exotherm for the epoxy casting system when 13TAN (an adduct of 1 mole of TETA with 3 mole of AN) was used as hardener. Moreover, their neat resin casting provides good mechanical properties without significant loss of thermal stability as compared to either of TETA, 11TAN, or 12TAN cured matrix system. The evaluation of laminates suggests the suitability of DGEBA-epoxy/ 13TAN resin system to provide a glass fabric/epoxy prepreg system with a shelf life of one month at −5°C for the fabrication of laminates.

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