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Advanced Fibre-Reinforced (Methyl) Nadicimide Resins*

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ABSTRACT

Glass/carbon/kevlar-reinforced composites were fabricated using two structurally different methyl nadicimide resins. The resin content of the laminates was in the range of 32-39 per cent. Interlaminar shear strength (ILSS) and flexural strength (FS) depended on the structure of the methyl nadicimide resins. A significant decrease in the ILSS was observed on treatment with boiling water for 500 h and on isothermal ageing at 300 °C for 100, 250 and 500 h. The limiting oxygen index (LOI) was the lowest for laminates based on kevlar fabrics (i.e. 54), whereas the laminates based on glass/carbon showed very high LOI (>90).

1. INTRODUCTION

The addition of a reinforcement (particulate or fibrous) to polymers can dramatically improve their performance and increase the area of their applications. Composite materials thus obtained have great potential in diverse areas ranging from transportation (aerospace, land and marine) to construction and dental and medical prosthesis. The mechanical properties of these composite materials depend on the (i) volume fraction, orientation and nature of the reinforcement, (ii) degree of interfacial adhesion, and (iii) nature of polymer matrix.

The role of matrix is manifold in a composite. It binds the fibres together and protects them from abrasion. Matrix is also the major factor in damage tolerance of the composites. The ability of the polymer matrix to undergo plastic flow either homogeneously or inhomogeneously in the form of shear bending and/or crazing is the major factor associated with composite toughness and performance. To minimise the composite failure by buckling, the matrix has to be stiff also.

A wide variety of thermosets, e.g., epoxies, maleimides, nadicimides and acetylene terminated imides, toughened thermoset and thermoplastic polymers have been used as matrices in composite materials[1-3]. Epoxies have dominated the scene and account for 90 per cent of the resins used in advanced composites. This is because of their ease of processability and excellent room temperature properties. One of the major limitations of epoxies is their poor performance in hot-wet environment. The maleimide/nadicimide end-capped oligomers/ monomers on curing give highly crosslinked, void-free network polymers having good retention of physical properties in hot-wet environment. These monomers/oligomers have been extensively investigated as matrix resins for the fabrication of advanced fibre-reinforced composites, which can be

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successfully used (for shorter or longer duration) at temperatures above 250 °C.

Although, considerable work has been reported on maleimide/nadicimide[4], studies on advanced fibre-reinforced composites based on methyl nadicimide matrices have not been reported. Therefore, in the present work, the attention has been focussed on glass/carbon/kevlar fibre-reinforced methyl nadicimide composites.

Most of the maleimides/nadicimides are soluble in high boiling solvents (e.g. DMF, DMAc, NMP etc.) which have a tendency to remain associated with the polar groups of the matrix resins. This polymer-bound solvent is either removed at high temperatures generally used in the processing of the laminates, thereby creating voids or it acts as a plasticiser thereby affecting the high temperature performance of the laminate. There is, therefore, a need to develop nadicimide resins soluble in low boiling solvents. The methyl nadicimides synthesised in our laboratory were found to be soluble in low boiling solvent like acetone and methyl ethyl ketone[5]. The fabrication of laminate therefore could be done using methyl ethyl ketone.

The transmission of stress between fibre and matrix depends on a strong interfacial bond which resists failure[6,7]. For this reason, the degree of contact and the cohesive forces at the interface are of considerable importance[8]. The interfacial bonding is crucial because a major failure mechanism is the growth of cracks between fibre reinforcement and matrix resin, that holds the material together. The interfacial bond can influence various aspects of composite behaviour, such as composite strength, modes of failure, Young's modulus, interlaminar shear strength (ILSS), bending stiffness, and compressive strength.

Moisture has an adverse effect on adhesive bonding. Three general areas of water attack are: (i) the oxide surface of the adherend (in the case of glass/carbon fibres), (ii) the polymer immediately adjacent to the adherend, and (iii) bulk polymer away from the interface. Interfacial and bulk polymers are distinguished since the polymer near the adherend may have a different structure from that of the bulk polymer. The deterioration may be reversible or irreversible. The lowering of Tg due to plasticisation of matrix material in the presence of water is reversible if sorbed moisture is removed without causing damage to matrix. However, if the fibre matrix interfacial shear strength is affected, the damage is irreversible. Therefore, heat ageing studies on glass/carbon/kevlar-reinforced methyl nadicimides were carried out at 300 °C for several hours (100-500 h) and the effect of thermal ageing on ILSS was investigated. Exposure to hygrothermal ageing on ILSS was also investigated.

2. EXPERIMENTAL

2.1 Materials

The reinforcements, i.e., E-glass fabric 8H satin weave (300 g/m^2, Unnati Corporation, Ahmedabad, density 2.54 g/cm^3), carbon fabric, plain weave (200 g/m^2, Torayaca, density 1.70 g/cm^3) and kevlar-29 fabric plain weave (460 g/m^2, Barstrex, Germany, density 1.44 g/cm^3) were used as received.

The methyl nadicimide resins in amide-acid form were used for composite fabrication and were synthesised in the laboratory by reacting methyl nadic anhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA)/pyromellitic dianhydride with tris(3-aminophenyl)phosphine oxide using glacial acetic acid and acetone as solvents as reported earlier[8]

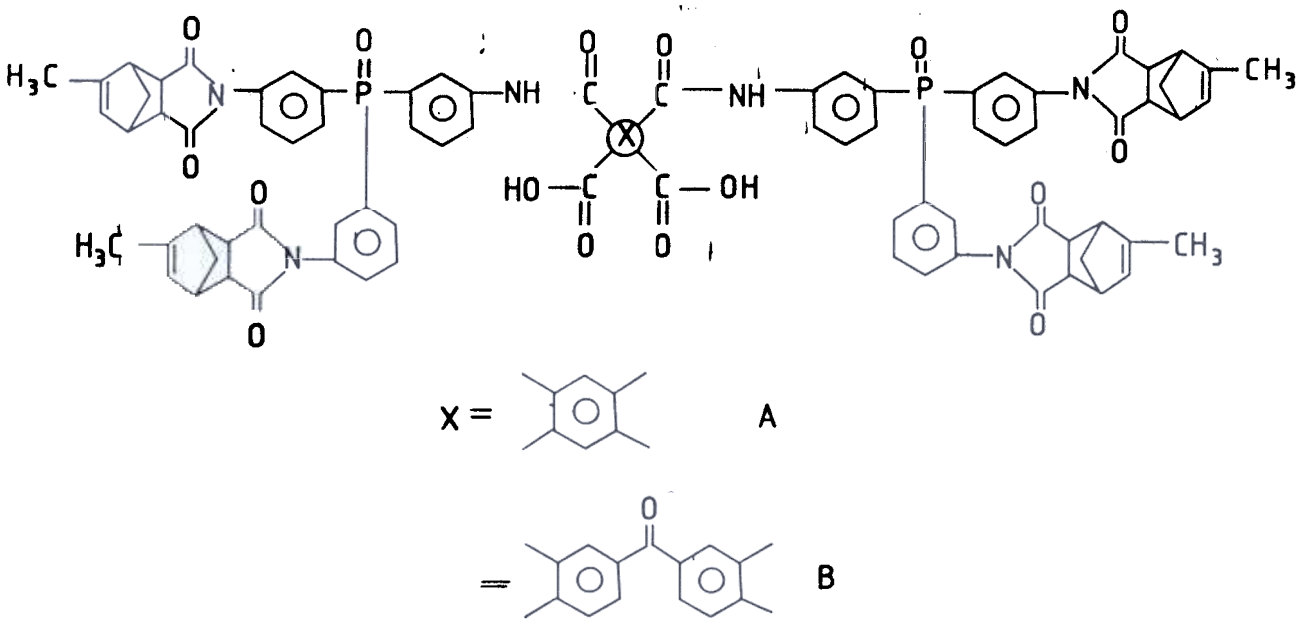
The chemical structure of these resins can be depicted as shown in Structure I opposite.

2.2 Composite Fabrication

Approximately 40 per cent solution (w/w) of resin matrices A/B was prepared in methyl ethyl ketone. Ten plies of 6 in. × 6 in. glass fabric and eight plies of 6 in. × 6 in. carbon fabric/kevlar-29 were coated with this solution. The prepregs were dried in air oven at 80 °C for 1 h. The dried prepregs were stacked together and placed in an oven at 150 °C for 1 h under reduced pressure to carry out imidisation of the resin. The stack was then placed between teflon sheets and mild steel plates, and the assembly inserted between preheated platens of Carver laboratory hydraulic press maintained at 260 °C. A pressure of 3.16 MPa was applied and the pressure and temperature were maintained for 2 h. The press was then switched off and when the temperature of the platens was below 50 °C, the pressure was released and the laminate was taken out. Post-curing was done at 325 °C for 8 h.

2.3 Composite Characterisation

Density of resin was determined by suspension method using methanol and chloroform as solvent. The



Structure I

density of the composite was determined by water displacement method (ASTM D-792).

Resin content of the glass fibre-reinforced methyl nadicimide was evaluated by pyrolysis method. For this purpose weighed pieces of the laminate (0.25 in. × 0.25 in.) were placed in an uncovered silica crucible which was heated in a furnace at 600 °C for 2 h. The resin was completely burnt off at this temperature, but the glass fibres remained unaffected. After cooling, the crucible was weighed and the weight of the fibres was determined. In the case of kevlar/carbon fibre-reinforced composites, the weighed quantity (0.3 g) of the laminate was treated with hydrazine hydrate at slightly elevated temperature (50 °C) in a beaker till the methyl nadicimide dissolved leaving the fibres behind (2 h). The fibres were then washed with acetone several times and then filtered using a preweighed sintered glass crucible (grade-3), and dried. The weight of the fibres was determined and the resin content of the test specimen was calculated.

The void content of the laminates was calculated from the experimental density ρ_{ce} of the composite and the theoretical density (ρ_{ct}).

$$\text{Void (\%)} = \frac{\rho_{ct} - \rho_{ce}}{\rho_{ct}}$$

Flammability characteristics of the laminates were obtained by finding the limiting oxygen index (LOI) according to ASTM D 2863-70 using Stanton Redcraft FTA flammability unit.

The flexural strength (FS) was determined according to ASTM D 790-71 using Instron tensile testing machine model 1112. A three-point loading system utilising centre loading on a supported beam (width-13-14 mm) was used. The test parameters employed were : support span-to-depth ratio = 32:1, crosshead speed = 0 mm/min, chart speed = 200 mm/min.

Interlaminar shear strength was determined according to ASTM D 2344-76 (using samples of size 13-15 mm length and 12-14 mm width). A chart speed of 50 mm/min, crosshead speed of 1 mm/min, span-to-depth ratio of 5:1 and length-to-depth ratio of 7:1 were used.

For hygrothermal and oven ageing of laminates, pieces of dimensions 0.5 in. × 0.4 in. were accurately weighed and placed in boiling water for different intervals of time. Thermal ageing was done by heating 0.5 in. × 0.4 in. of the samples in a muffle furnace at 300 °C. The change in the weight and dimension was noted after regular intervals.

3. RESULTS AND DISCUSSION

The DSC scan of resins A and B showed exothermic transition due to curing in the temperature

range of 260-350 °C and 270-350 °C, respectively. Since the curing exotherm was above 250 °C for these (methyl) nadicimides, it was decided to fabricate laminates at a temperature of 260 °C (2 h) and post-curing at 325 °C (8 h). The density of cured resins A and B was found to be 1.35 and 1.34 g/cm^3, respectively.

The fabrication of glass/carbon/kevlar fabric-reinforced composites based on methyl nadicimides A and B (in amide acid form) was done using methyl ethyl ketone as a solvent. The prepregs had good tack and drape and could be easily processed. The laminate thickness and the volume fraction of the resin along with sample designations are summarised in Table 1.

Table 1. Fabrication of composites using glass/carbon/kevlar & resin A/B

Fibre	Matrix	Sample designation	Volume fraction of resin(%)	Laminate thickness (mm)
Glass	A	A-G	35	1.26-1.27
Glass	B	B-G	33	1.26-1.28
Carbon	A	A-C	39	1.32-1.34
Carbon	B	B-C	38	1.22-1.34
Kevlar	A	A-K	34	1.28-1.34
Kevlar	B	B-K	32	1.34-1.36

In Table 2, the density of the composite and void content are given.

Table 2. Density and void content of the laminates

Sample designation	Density Experimental	Theoretical	Void content (%)
A-G	2.08		1.92
B-G	1.79		2.20
A-C	1.38		2.80
B-C	1.24		4.00
A-K	1.24		3.70
B-K	1.19		4.00

Considerable work has been reported in recent years on composite fabrication using PMR resins. However, recent studies on preformed nadicimide end-capped resins-based composites are relatively few. Graphite woven cloth reinforced nadicimide resins have shown tensile strength (0.86 GPa), FS (1.01 GPa) and flexural modulus (53.78 GPa)[9].

Table 3 gives FS and ILSS of the laminates. The FS decreased in the following manner A-C > B-C > A-G > B-G > A-K > B-K. A similar trend was observed in flexural modulus and ILSS also. ILSS depends on interfacial adhesion of the matrix and the fibres. The maximum value of ILSS was in A-based laminates (A-G, A-C and A-K). This may be due to high number of polar imide groups per unit weight in these resins. The interaction of polar groups of the matrix with surface hydroxyl, *-C-O-C, >C=O, -CO$_2$* may account for this behaviour.

The LOI of the glass/carbon/kevlar-reinforced methyl nadicimides are summarised in Table 3.

Table 3. Mechanical properties & LOI of unaged glass/carbon/kevlar reinforced methyl nadicimides

Sample designation	Flexural strength(MPa)	Flexural modulus(GPa)	ILSS (MPa)	LOI
A-G	674	71.4	49.0	98.6
B-G	623	66.5	36.6	>98.1
A-C	763	75.0	66.0	>98.5
B-C	675	71.0	55.0	98.1
A-K	563	67.0	40.4	50.1
B-K	560	57.0	37.4	52.1

The samples were treated with boiling water for 100 h, 250 h and 500 h. No significant change in weight or dimension was observed on such a treatment. The moisture uptake tendency of these laminates was extremely low. However, there was a significant decrease in ILSS on such a treatment (Table 4).

Table 4. Effect of boiling water treatment on ILSS of glass/carbon/kevlar-reinforced methyl nadicimides

Sample designation	ILSS (MPa) after 100 h	250 h	500 h
A-G	30.9	20.4	19.0
B-G	28.5	27.4	15.3
A-C	46.0	38.0	29.0
B-C	28.6	25.0	17.4
A-K	29.4	14.4	12.7
B-K	25.2	21.6	16.5

The plot of per cent decrease in ILSS vs duration of boiling water treatment is given in Fig. 1. The decrease was maximum for B-C laminates (after 100 h 48 per cent and after 500 h 68 per cent), whereas after 250 h, the laminate A-K showed maximum decrease (64 per cent).

On heating the laminates in the furnace at 300 °C for 100 h, 250 h and 500 h, loss in weight for most of the laminates was observed (Table 5).

Table 5. Weight loss on isothermal ageing at 300 °C

Composite designation	Weight loss (%) after 100 h	250 h	500 h
A-G	1.1	2.4	
B-G	1.6	3.1	
A-C	1.0	2.1	
B-C	1.5	4.5	
A-K	1.3	2.9	
B-K	1.6	3.4	

Lower weight loss after 100 h, 250 h and 500 h was observed for laminates A-G, A-C, A-K. The weight loss on 500 h exposure was more than the 250 h and 100 h exposures.

All samples showed a decrease in ILSS on thermal ageing at 300 °C, thereby indicating oxidative degradation. Plot of per cent decrease in ILSS vs time of exposure is given in Fig. 2. These studies

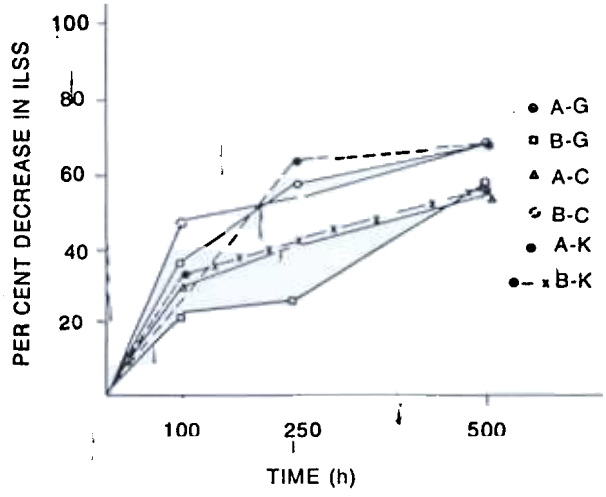


Figure 1. Plot of per cent decrease in ILSS vs duration of hygro-thermal ageing.

thus indicate that methyl nadicimides can be used as matrix resins in advanced fibre (i.e. glass, kevlar or carbon)-reinforced composites. These resins are soluble in low boiling solvents (methyl ethyl ketone) thereby facilitating the processing.

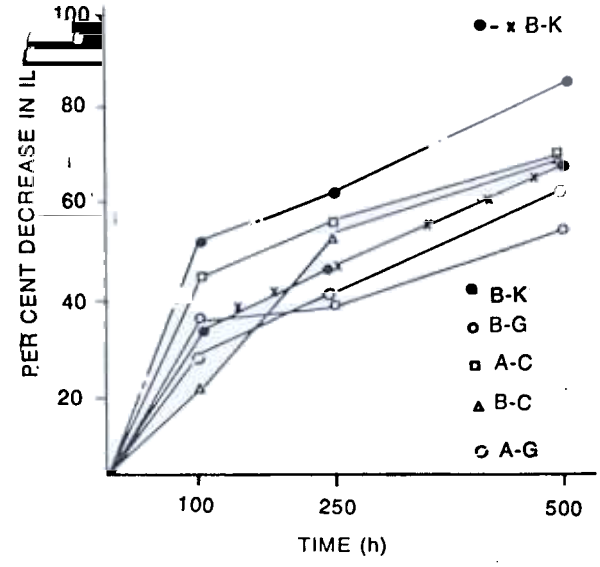


Figure 2. Plot of per cent decrease in ILSS vs time of exposure.

REFERENCES

1. Serafini, T.T.; Delvigs, P. & Lightsey, G.R. *J. Appl. Polym. Sci.*, 1971, **16**, 90-95.
2. Delvigs, P.; Serafini, T.T. & Lightsey, G.R. Proceedings of 17th SAMPE National Symposium, April 1972.
3. Serafini, T.T.; Delvigs, P. & Alston, W.B. Proceedings of 27th SAMPE National Symposium, May 1982.
4. Srivastava, Anju & Varma, I.K. *In* Polymer Sciences, Recent Advances, edited by I.S. Bhardwaj. Proceedings of the National Conference on Polymer-94, 8-10 February 1994, Vadodara. Allied Publisher, New Delhi, 1994. pp. 673-81.
5. Sarfaraz Alam; Kandpal, L.D. & Varma, I.K. Methyl nadicimide resins: Synthesis and characterisation. *J. Appl. Polym. Sci.*, 1994, **53**, 1073-81.
6. Danksys, R.J. *J. Adhesion*, 1973, **5**, 13.
7. Daelble, D.H.; Dynes, P.J. & Cirlin, E.H. *J. Adhesion*, 1974, **6**, 23-27.
8. Broutman, L.J. & Krock, R.H. Composite Materials. Academic Press, New York, 1974. pp. 6-8.
9. Lee, Y.D. & Ting, M.I. *J. Appl. Polym. Sci.*, 1990, **41**, 2177.

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