

Effect of structure of nadimides on properties of glass fibre reinforced composites*

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Received 11 October 2000; accepted 1 March 2001

The paper describes fabrication of glass fibre reinforced laminates based on three structurally different nadimide oligomers containing phosphine oxide in the backbone and a low molecular weight low viscosity allyl nadicimide resin. Fabrication of laminates was done using methyl ethyl ketone solvent. Interlaminar shear strength and flexural strength of laminates, containing 0.67-0.5 volume fraction of fibres, depended on the structure of the resin and was found to be higher in laminates based on resins with higher polarity and having phosphine oxide in backbone. Properties of composites based on blends of these resins could be predicted on the basis of rule of mixtures. A marginal synergism was observed in one case. T_g was in the range of 230-270°C and was found to increase marginally in blends. Effect of oven aging and boiling water treatment on the properties of composites is also reported.

Several thermoset matrix resins (e.g. epoxies, maleimides, nadimides) have been used in the fabrication of advanced fibre reinforced composites¹. Epoxies have dominated the scene and account for 80-90% of the resins used in advanced fibre reinforced composites because of the ease of processability and excellent room temperature properties. However, their use temperature is limited to 177°C due to poor resistance to hot-wet environment.

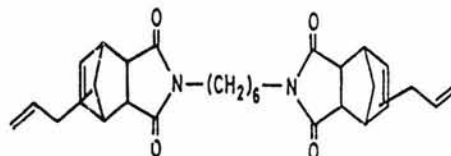
The nadimide end-capped oligomers/monomers on curing give highly crosslinked, void free network polymers having good physical properties and outstanding thermal stability and lower water absorption than the currently used epoxy systems. They can be used at temperatures greater than 300°C. We have earlier reported curing behaviour and thermal stability of nadimide resins^{2,3} prepared in our laboratories. Thermal behaviour of blends of nadimides and commercially available allyl nadicimides has also been reported⁴. Incorporation of phosphorus in the nadimide backbone increased the anaerobic char yields of the cured resins. Polymers having higher char residue generally have better flame resistance characteristics. van Krevelen⁵ has suggested a direct relationship between limiting oxygen index and char residue of polymers at 800°C.

Composites based on phosphorus containing nadimide resins, therefore, are expected to have improved flame resistance characteristics.

In this paper, studies pertaining to the effect of structure of nadimides on their glass fibre reinforced laminates are described. Glass transition temperature (T_g), interlaminar shear strength and flexural strength of the composites were determined. The effects of heat aging and hygrothermal aging on interlaminar shear strength were also evaluated.

Experimental Procedure

Materials—Allyl nadicimide resin, (V), based on hexamethylene diamine was procured from CIBA GEIGY⁶ and had the following structure :

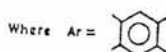
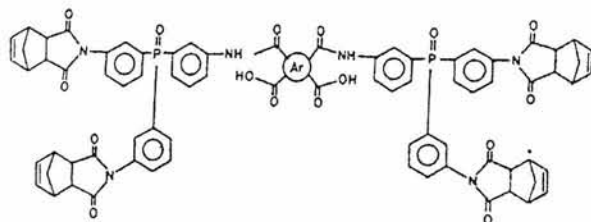


Phosphorus containing nadimide resins having following structures were prepared according to the method reported elsewhere^{2,3}.

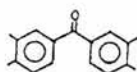
Epoxy compatible E-glass fabric RP-8 (density 280 g/m²) of Pilkington Fibre glass co. was used as reinforcement.

Composite Fabrication—The procedure used for fabrication of composites, based on methyl ethyl ketone solutions of resin P, B, F and resin V (40%

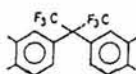
*Part of this paper was presented at Polymers 94, Vadodara, India.



Resin
designation
P



B



F

w/w) and their blends was different from each other. Therefore, the three methods of composite fabrication are described separately.

Ten pieces of 6" × 6" glass fabric were coated with the resin V solution. The prepreps were dried at room temperature and then in an air oven at 80 °C for 1-2 h. The stack of dried prepreps was inserted directly into the heated platens of compression molding machine maintained at 150 °C. No pressure was applied at this stage. The temperature was maintained for 2 h, and then slowly raised to 200°C and a pressure of 3.16 MPa was applied at this temperature. Pressure and temperature were maintained for 2 h. The temperature was further increased to 260°C at the same pressure, and maintained for 2 h. The press was then switched off and when the temperature of platens was below 50°C, pressure was released and laminate removed from the press.

For the fabrication of composites from resins P, B, F, coating and drying of prepreps was done similar to that described for resin matrix V. The dried prepreps were stacked together and placed in a vacuum oven at 150°C for 1 h in order to carry out imidisation of the resin. The stack was 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.

The blends of nadimides : allyl nadicimide (1:1 w/w) were used to coat the glass fabric. The prepreps, after drying, were subjected to thermal imidisation at 150°C for 1 h in vacuum oven. The stack was placed between teflon sheets and mild steel plates and the assembly inserted between platens of hydraulic press preheated to 200°C. No pressure was applied and temperature was maintained for 1 h. The temperature was raised slowly to 260°C and a pressure of 3.16 MPa was applied and maintained for 2 h. The laminate was then allowed to cool to 50°C while still under pressure. It was then removed from the press after releasing the pressure.

Determination of Density of Resins and Laminates—Density of cured nadimide resins was determined by suspension method using methanol and chloroform solvents, and of composite was determined by water displacement method using specific gravity bottle.

Determination of Resin Content—Resin content of the laminates was determined using hydrazine hydrate method. A weighed quantity (~0.3 g) of the laminate was heated in hydrazine hydrate in a beaker till the nadimide dissolved leaving the glass fibres behind (~2 h). The fibres were washed with acetone several times and then filtered using a preweighed dry sintered glass crucible (grade -3), and dried. The resin content of the test specimen (w/w) was calculated from a knowledge of the weight of the fibre, composite and resins. Since the density of the constituents was determined (or known) the volume fraction of the fibres could be evaluated according to the formula :

$$\text{Volume fraction of fibres (v}_f\text{)} = \frac{w_f / \rho_f}{(w_r / \rho_r + w_f / \rho_f)}$$

Determination of mechanical properties—Flexural strength and flexural modulus of the laminates was determined according to ASTM D790-71 using Instron tensile testing machine model 1112. A three point loading system utilising the centre loading on a supported beam was used. Interlaminar shear strength (ILSS) was determined according to ASTM D2344-76. Five specimens were tested for each sample and their average has been reported.

Hygrothermal and oven aging of Laminates—Laminate pieces of dimensions 0.5" × 0.4" were accurately weighed and placed in boiling water for different intervals of time. Similarly 0.5" × 0.4 " of the composites were heated in muffle furnace at 300°C. The change in weight and dimension were

noted after regular intervals of time. ILSS of the samples aged under these conditions was determined.

Dynamic Mechanical Thermal Analysis—Dynamic mechanical thermal analysis of laminates was done using Polymer Laboratories MK II dynamic mechanical thermal analyser. The experiment was carried out in the temperature range of 50-300°C. Heating rate of 5°C/min and frequency of 1 and 10 Hz was maintained.

Results and Discussion

One of the problems associated with most of the addition polyimides is their poor solubility in low boiling solvents. The processing in such cases has to be done using high boiling solvents (eg. DMF, DMAc, NMP etc.) which have a tendency to remain associated with the polar groups of the matrix resins (i.e. imide group of nadimide resins). This polymer bound solvent is either removed at the 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 laminates. In the nadimides investigated here, such a problem did not exist because of their solubility in low boiling solvents like methyl ethyl ketone or acetone. The fabrication of laminates from these resins could, therefore, be easily done using these low boiling solvents. The prepregs had good tack and drape characteristics.

Since the curing exotherm, as studied in DSC scans, was above 250°C for these nadimides²⁻⁴, it was decided to fabricate laminates by using a temperature of 260°C for 2 h. The allyl nadicimide resin was of lower viscosity and cured slowly, hence a longer cure cycle was used for this matrix. The advancement of resin was done by heating the laminates at 200°C for 2 h before increasing the temperature to 260°C.

Table 1 gives the flexural strength and ILSS values along with resin content of the laminates. The volume fraction of the fibres was in the range of 0.67-0.59. ILSS depends on the interfacial adhesion of the matrix and the fibres. In glass fibres, polar groups (-OH) are present on the surface and if the matrix is also polar then one can expect better interaction between the two constituents. The formulated molecular weight of imidised resins based on V, P, B and F is 478, 1412, 1516 and 1638 respectively. The polarity in these resins may be attributed to the imide groups as well as presence of phosphine oxide groups. The imide group per formulated molecular weight is 239 (478/2), 235 (1412/6), 252 (1516/6) and 273 (1638/6) respectively. The imide content is highest in

P followed by V, B and F. The ILSS therefore is expected to be maximum in 'P' based laminates and this is supported by our results. However, the ILSS was lowest in laminates based on resin V and this may be due to lack of phosphine oxide groups in this resin (Fig. 1). The presence of C=O group in resin B may be also a contributing factor for increasing ILSS of these laminates. In the laminates fabricated using blends of P, B and F with resin V, the mechanical properties may be predicted on the basis of rule of mixtures. The flexural strength and ILSS predicted on this basis are also reported in Table 1. These results show a synergistic effect in laminates based on resin B.

Table 2 gives the storage modulus of the composites at 1 Hz and 10 Hz. Temperature at which the composites begin to soften is also indicated (obtained by extrapolation of tangents to the steepest portion of the storage modulus curve). The softening temperature of pure nadimide and allyl nadicimide lie in the range of 233- 252°C (Fig.2). On blending, these values increase by 20-30°C. This increase in T_g in the blends shows the formation of a rigid network on co-curing of these resin blends. However, formation of such a rigid network is not supported by the results of flexural modulus of the laminates. Modulus of the

Table 1—Mechanical properties and resin content of glass fibre reinforced nadimides

Lami- nates based on resins	Resin content (vol%)	Flexural strength (MPa)	Flexural modulus (GPa)	ILSS (MPa)
P	37	609	61	70
B	33	526	60	48
F	33	537	61	44
V	39	496	61	33
P+V	40	552 (555)	55	48(51.2)
B+V	41	641 (511)	63	49(40.5)
F+V	40	517 (517)	58	39(38.5)

Figures in parantheses indicate the calculated values based on rule of mixtures.

Table 2—Storage modulus and softening temperatures of glass fibre reinforced nadimides

Laminates based on resins	Log E' at 100°C		Softening temperature (°C)
	1 Hz	10Hz	
P	6.2708	6.2708	233
B	6.2083	6.2083	247
F	6.2014	6.2083	252
V	6.0417	6.0417	243
P+V	5.9931	6.0486	266
B+V	6.0625	6.0625	272
F+V	6.2083	6.2153	270

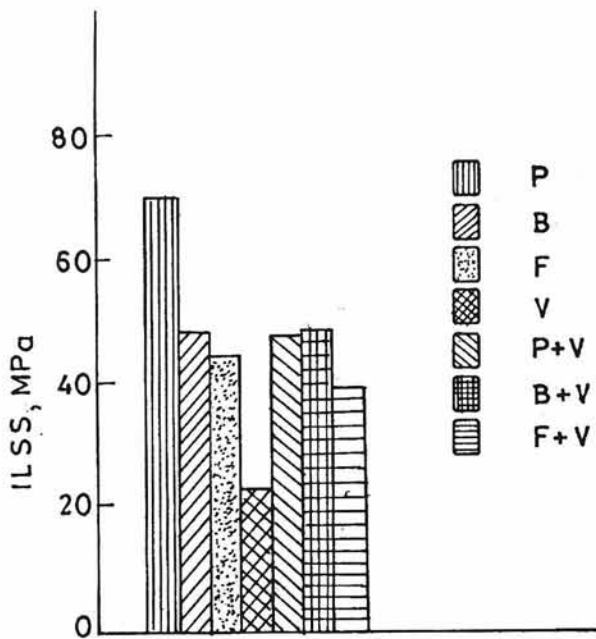


Fig. 1—Room temperature interlaminar shear strength of glass fibre reinforced nadimides /allyl nadicimides.

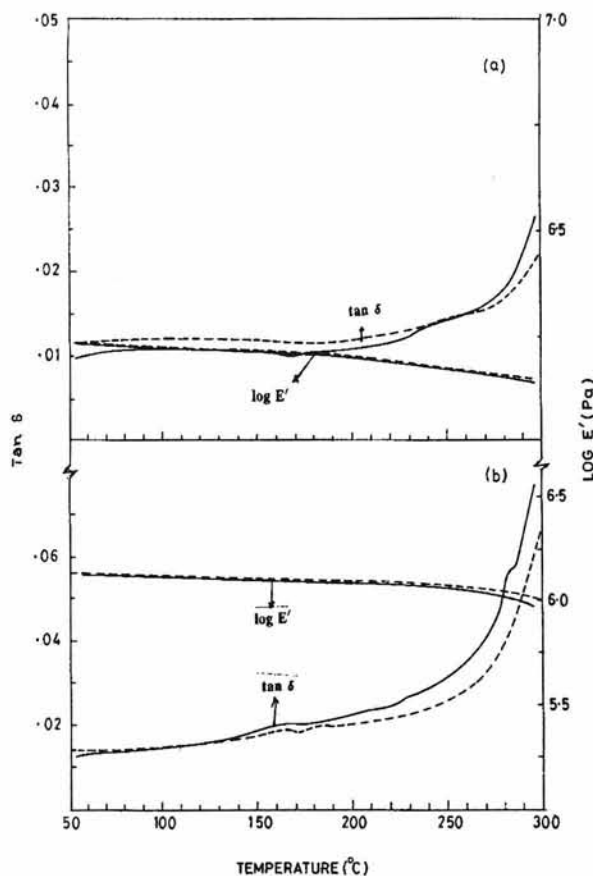


Fig. 2—DMTA trace of glass fibre reinforced laminates based on resin (a) B (b) B + V (— 1 Hz) (----- 10 Hz)

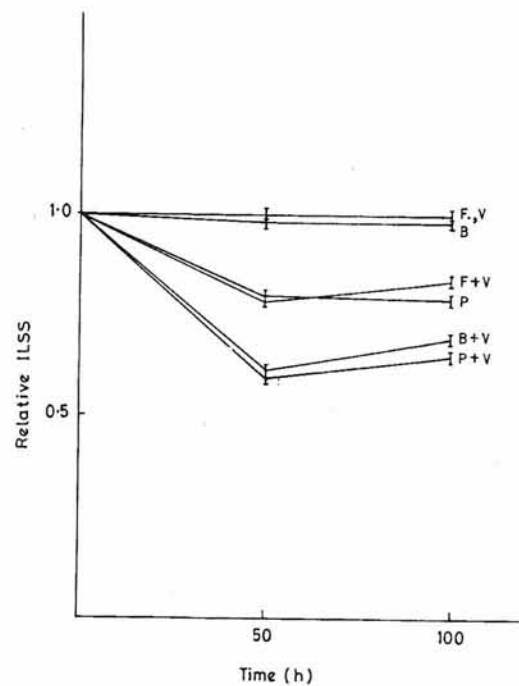


Fig. 3—Plots of relative change in ILSS versus time of exposure to hydrothermal aging.

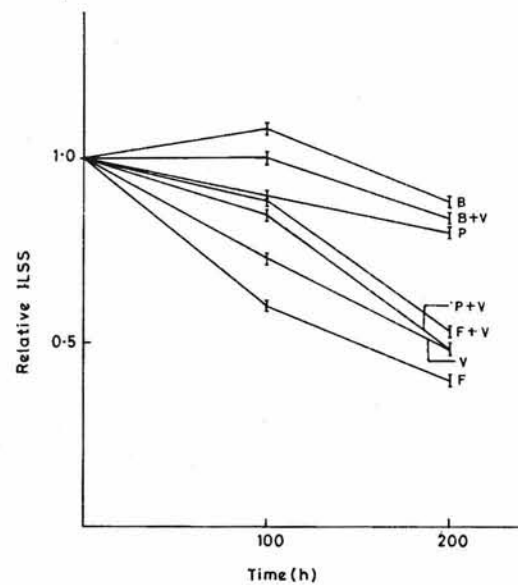


Fig. 4—Plots of relative change in ILSS versus time of exposure to oven aging at 300°C.

laminates also depends on the interfacial bonding and wetting of the fibre by the matrix resin.

The samples were treated with boiling water for 50 h and 100 h. It was found that no significant change in weight or dimension takes place on such a treatment. Thus, the moisture uptake tendency of these laminates

Table 3—ILSS of glass fibre reinforced nadimides after keeping in boiling water

Laminates based on resin	ILSS (MPa)	
	50 h	100 h
P	56	55
B	47	47
F	44	44
V	34	34
P+V	29	31
B+V	30	34
F+V	30	32

Table 4—Results of weight loss and ILSS on oven aging (300°C) of glass fibre reinforced nadimides

Laminates based on resin	Weight Loss (%)		ILSS (MPa)	
	100 h	200 h	100 h	200 h
P	1.0-3.0	1.7-2.2	63	56
B	1.0-2.0	2.6-4.1	52	42
F	2.4-3.3	4.4-5.8	26	18
V	3.0-4.0	6.4-8.7	24	16
P+V	1.4-2.2	1.5-6.0	41	23
B+V	1.8-2.4	2.8-3.5	49	40
F+V	1.6-2.2	5.0-6.4	34	20

is extremely low. However, there was a decrease in ILSS on such a treatment (Table 3). The decrease was maximum in P based samples. Only a marginal decrease in ILSS was observed for B, F and V based composites. On blending, the maximum decrease in ILSS was in blends of resin P followed by B and F. Plots of relative change in ILSS (taken as ratio of ILSS of aged and unaged sample) versus duration of boiling water treatment is given in Fig.3.

On heating the laminates in the furnace at 300°C for 100 h and 200 h loss in weight for most of the laminates was observed (Table 4). The weight loss on 200 h exposure was more than the 100 h exposure. ILSS of the aged samples is given in Table 4. Except for composite from resin 'B' all others show a decrease in ILSS on aging at 300°C for 100 h thereby indicating oxidative degradation. In resin B, ILSS increased initially. On exposure for 200 h, a decrease in interlaminar shear strength in all laminates was observed. Plots of relative change in ILSS versus time of heating are given in Fig. 4. Composites based on resin B and its blends with resin V can therefore be used conveniently upto 100 h at 300°C.

These results show an improvement in the interlaminar shear strength of composites based on nadimide resins having higher polarity and phosphine oxide in the backbone.

References

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