

Polyarylacetylene Blends with Improved Processability and High Thermal Stability

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ABSTRACT: Novel binary blends of polyarylacetylene (PAA resin) with propargyl-novolac resin (PN resin) was prepared. The miscibility, processing capability, and thermal properties of the blends were investigated. The evaluation of the blends as matrices for thermostructural composites was also studied. The blends were highly miscible. In comparison to PAA resin, the blends exhibited remarkably improved processability suitable to various process techniques (especially resin transfer molding, RTM). By dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), it was revealed that the cured blends

possessed high thermal stability. The blend with 1/2 PN content was evaluated as matrices. The high temperature mechanical properties of silica laminates were compared favorably with those of conventional phenolic laminate. When compared with pure PAA laminate, the blend matrix laminate exhibited improved mechanical properties at both ambient temperature and high temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2939–2946, 2007

Key words: resins; blends; processing; thermal properties; mechanical properties

INTRODUCTION

Polyarylacetylene resin [PAA, Fig. 1(a)] has been regarded as the best alternate to phenolic resin for matrices in high temperature composite materials.¹ PAA resin is polyphenylene oligomer^{2,3} that contains only carbon and hydrogen. Cured PAA is a highly crosslinked aromatic material with very high T_g (above the temperature of decomposition), and its char yield at 900°C in nitrogen is ~90% (that is, much higher than the corresponding value of ~60% for phenolic resin).⁴ PAA resin as HA43 by Hercules was available in the late 1970s.⁵ In 1980s, to obviate the problems of large amount of heat and severe shrinkage upon cure, Katzman et al.¹ developed a controllable, low temperature prepolymerization technique that produced a soluble, easy-to-process PAA oligomer. The ablative performance of carbon fabric/PAA composites was marginally improved in comparison to that of conventional phenolics composites.¹

High temperature resins presently available have various drawbacks, which limit their utilization in many applications. A serious one frequently encountered is the evolution of volatile during the processing. For example, when phenolic resins are cured, water or ammonia is released causing void formation, which makes it imperative that the entire cure be

carried out under high pressure.^{6,7} But PAA resin can be shaped without gas evolution during thermal cure, and this characteristic makes PAA suitable to low pressure process techniques, especially resin transfer molding (RTM), which is regarded as revolutionary process in composites fabrication.

However, there are still three main shortcomings for PAA resin:^{2–5}

1. the cure exothermic heat is higher than 1000 J/g, and the curing speed is so fast that it can explode during processing;
2. the mechanical properties of PAA composites are comparably poor, especially the interlaminar shear strength (ILSS); the composites are brittle and have poor structural integrity;
3. the cost of PAA resin is extraordinarily high.

Polymer blending has been applied as an efficient method to improve the performances of various polymers.⁸ The major concerns in composite matrix area are to strengthen the mechanical property⁹ and thermal resistance.¹⁰ Here again, we found that those deficiencies of PAA resin could be well overcome by blending with propargyl-novolac resin [PN resin, Fig. 1(b)]—a novel addition-cure phenolic resin.

PN resin possesses excellent processability, its cured material is thermally stable and its composites exhibited high mechanical and thermal properties.¹¹ It can be polymerized via addition polymerization of ethynyl groups thermally or catalytically. PN resin can be processed under low pressure to give

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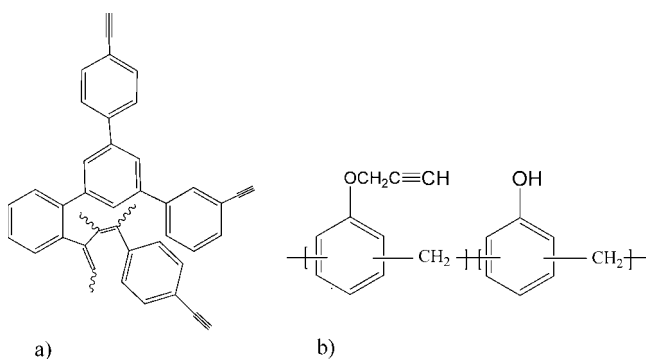


Figure 1 Molecular structures of ethynyl-containing resins: PAA and PN.

void-free materials.¹² Noticeably, the cost of PN resin is much lower than that of PAA resin.¹³

PN resin has the quality of conventional phenolic resin: low flammability, high char yield ($\sim 60\%$), ablative resistance (widely applied in ablative components in rockets and missiles), and low cost.^{14,15}

The work described here is to characterize the miscibility and processability of the binary blends of PN and PAA to investigate the thermal stability of the cured blend resins and to evaluate the blends as matrices for high temperature thermostructural composites. By introducing PN resin as a component into the PAA blend, there are three objectives that we hope to affect: (1) to improve the processing capability of PAA; (2) to improve the mechanical properties of the composite materials; and (3) to decrease the cost of the matrix resin.

EXPERIMENTAL

Materials

Novolac resin was prepared in our laboratory ($M_n = 576$ by ^1H NMR). Potassium hydroxide (A.R., Beijing Yili Chemicals Factory, People's Republic of China) and butanol (A.R., Beijing Yili Chemicals Factory, People's Republic of China) were used as received. Propargyl bromide (80 wt % toluene solution, Jiangsu Yangnong Company, People's Republic of China) was distilled before use. PAA resin was kindly provided by Aerospace Research Institute of Aerospace Materials and Processing Technology, China Aerospace Science and Technology.

Characterization methods

The chemical structures of the resins were elucidated by FTIR (PerkinElmer, IR2000) and ^1H NMR (Bruker, AV400) spectroscopic methods. FTIR spectra (KBr pellets) were averaged over 20 scans taken at 4 cm^{-1} resolution. Solution ^1H NMR spectra were recorded using $\text{DMSO-}d_6$ as solvent and tetramethylsilane (TMS) as internal standard. T_g and thermal cure were analyzed by nonisothermal DSC (Mettler-Toledo, DSC822^e) at a heating rate of $10^\circ\text{C}/\text{min}$ in a purging N_2 of $50\text{ mL}/\text{min}$. Rheological properties were determined by viscometer (NDJ-79 rotating viscometer) at different temperatures and various time intervals. Gel time was determined using a home-made apparatus according to China national standard GB-7193.1-1987. Thermal stability was evaluated by TGA on Netzsch STA409PC at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 flow of $30\text{ mL}/\text{min}$ and DMA on Netzsch DMA242C at a heating rate of $3^\circ\text{C}/\text{min}$ in N_2 flow of $50\text{ mL}/\text{min}$. The microstructure characteristics of the cured polymers were investigated by scanning electron microscopy (SEM, S-3000, Hitachi) and transfer electronic microscopy (TEM, H-800, Hitachi).

Synthesis of PN resin

The PN resin was synthesized by the Williamson reaction between novolac and propargyl bromide catalyzed by KOH in butanol solution.¹⁶ The synthetic scheme is shown in Figure 2. In a typical experimental, novolac (10.4 g, 0.1 mol) and butanol (12 mL) were placed in a three-necked flask equipped with a mechanical stirrer, a thermometer, and a condenser. After the mixture was stirred into a solution, KOH (5.33 g, 0.08 mol) was added. Until a purple solution was formed, propargyl bromide (9.52 g, 0.08 mol) was added dropwise under vigorous agitation over a period of 15 min at 70°C . The reaction was kept at 80°C for another 3 h till the mixture turned pale yellow and its pH value was about seven. After the precipitates were filtrated, the filtrate was washed with hot deionized water until the water phase was negative to Ag^+ ; then butanol was removed by rotary evaporation at 100°C to give a brown-red viscous resin. Thus, PN resin with $\sim 80\%$ propargyl content was prepared. Yield (11 g, 91.7%). IR (KBr) cm^{-1} 3400 ($-\text{OH}$), 3288 ($\equiv\text{C}-\text{H}$), 3033 (aromatic $\text{C}-\text{H}$), 2122 ($\text{C}\equiv\text{C}$); ^1H NMR (DMSO) δ 3.35–3.53 ($\equiv\text{C}-\text{H}$), 3.70–

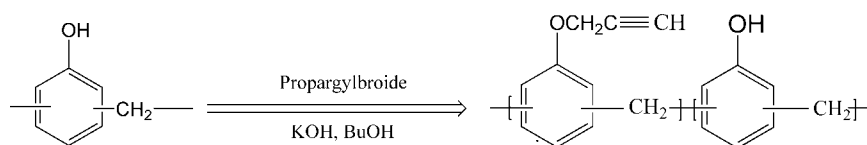


Figure 2 Synthesis of PN resin.

3.81 ($-\phi-CH_2-\phi-$), 4.7–4.8 ($-\text{OCH}_2\text{C}\equiv\text{C}-$), 6.6–7.3 (aromatic hydrogen).

Preparation of the blends

PN and PAA were weighed according to the designed composition of the blend. After heating at 70°C for 30 min, they were placed into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a condenser. The mixture was stirred vigorously at 70°C for 30 min to get the final blend.

According to the earlier procedure, the blends with PN weight contents of 1/3, 1/2, and 2/3 were prepared, and they were designated as PN-PAA (1 : 2), PN-PAA (1 : 1), and PN-PAA (2 : 1), respectively.

Thermal cure of the blends

The resins were cured in an electric convection oven as per the following protocol:

R.T. + @120°C for 1 h + @150°C for 2 h + @170°C for 1 h + @190°C for 1 h + @210°C for 3 h + @250°C for 4 h.

The completion of cure was manifested by FTIR spectra showing the entire disappearance of the characteristic peak of $\text{C}\equiv\text{C}$ at $\sim 2122\text{ cm}^{-1}$.

Preparation of silica laminates

Silica cloth was impregnated by the methylethylketone solution of PN-PAA (1 : 1) blend and dried under ambient conditions. The prepregs were stacked in a steel mold, and heated between two steel platens in a hydraulic press with a contact pressure at 150°C. After the resin flow was ceased, the plies were cured under 4 MPa pressure according to the following protocol: @150°C for 1 h, @170°C 1 h, @190°C 1 h, @210°C 3 h, and @250°C 4 h.

Laminate using conventional novolac phenolic resin as matrix was also prepared by the above-mentioned procedure.

The resin content of all laminates was kept at 30–36 wt %.

RESULTS AND DISCUSSION

Blend miscibility

Various degrees of miscibility are possible in polymer blends ranging from complete miscibility to phase separation.¹⁷ Miscibility is a function of the interaction of polymer molecules in the blend and can be detected using various methods.¹⁸ The properties of polymer blends are always governed by the miscibility of the components.¹⁹ Here, we characterized the miscibility of PN-PAA blend by appearance observation, DSC (T_g), indices of refraction (RI), SEM, and TEM techniques.

Over the whole experimental temperature range, the blends with varying PN contents all appeared transparent, implying that there was no visible phase separation in the melt, gel, and cured solid of the blends. In view that the indices of refraction of PAA and PN are different (at 30°C, RI for PAA is 1.6375 and for PN is 1.6127), the transparency is an indication of good miscibility of the blend components and the absence of phase separation during heating and thermal cure.²⁰

Glass transition analysis is a widely used technique to evaluate the miscibility of polymer blends.²¹ Figure 3 shows the DSC profiles of PN, PAA, and their blends, showing their glass transitions. The T_g of PN-PAA blends were all between those of pure PN and PAA. Furthermore, the temperature transitions of the blends were all as sharp as those of pure PN and PAA, indicating the good miscibility of the blends.

Figure 4(a) shows the SEM image of the fractured surface of the cured PN-PAA (1 : 1) blend, and Figure 4(b) shows its TEM image. It appears that the cured blend is one phase in the micrometer and nanometer ranges. It indicates that the good miscibility between PN and PAA has been achieved. The good miscibility might result from the molecular similarity of PN and PAA since they are both rich in aromatic structures and ethynyl groups.²²

Processing capability of the blends

The blend of PN-PAA (1 : 1) was taken as an example to characterize the processing capability of PAA blends. Solubility, rheology, and cure characteristics are the crucial processing parameters of a matrix resin for the preparation of composite materials.²³

The PAA blend is soluble in common low toxic solvents such as methylethylketone (MEK) and tetrahydrofuran (THF), etc. The MEK solution is suitable to prepare prepregs for laminate composite.

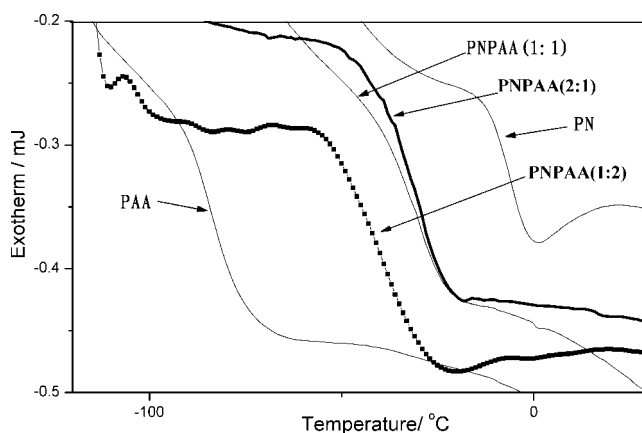


Figure 3 DSC profiles of PN, PAA, and PN-PAA blends (scanning rate 10°C/min; N_2 purging rate 50 mL/min).

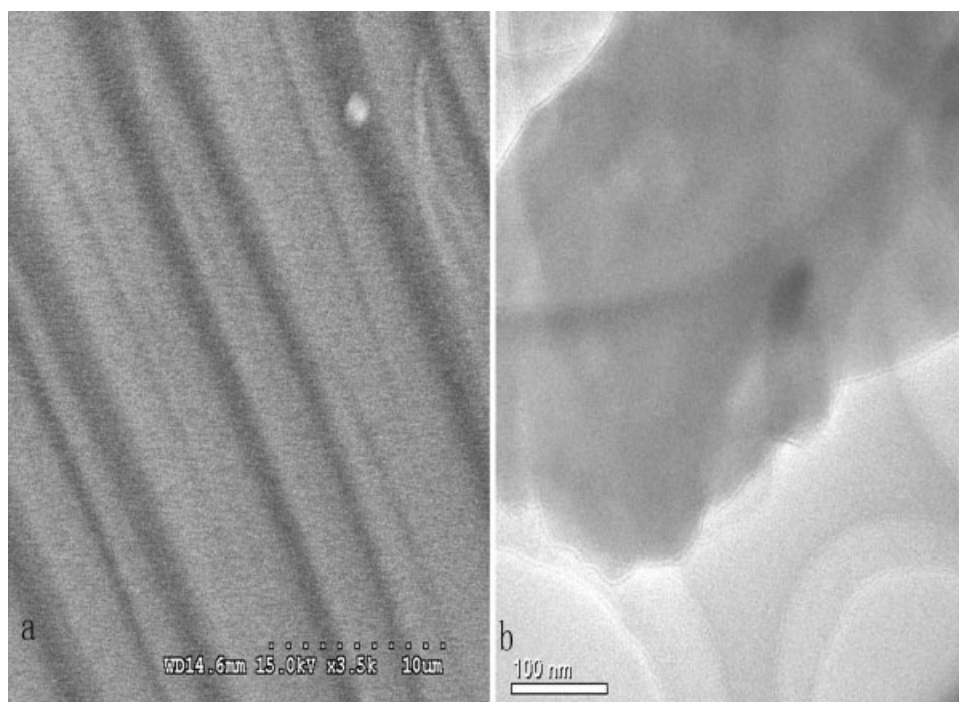


Figure 4 Morphology of the cured PN-PAA (1 : 1) blend (a) SEM ($\times 3.5$ K); (b) TEM ($\times 80$ K).

The temperature and time dependency of viscosities of PN-PAA (1 : 1) blend are shown in Figure 5. It is seen that (1) with increase in temperature, the viscosity decreases remarkably; (2) the viscosity is low enough for melt processing (lower than 200 MPa s at 90°C); and (3) the low viscosity can be maintained for at least 5 h. These results indicated that the PN-PAA blends are suitable for RTM process. In fact, the blend can be processed in various techniques (melt prepreg, solution prepreg, winding, etc.).

Thermal curing characteristics can be determined by DSC and gelation methods. DSC profiles in Figure 6 show a well-defined exotherm for the PN-PAA (1 : 1) blend, with an onset temperature at around 150°C , a peak temperature at around 230°C and an end temperature at around 300°C . These results indicate the presence of copolymerization between PN and PAA, because the cure exotherms of the two pure polymers are quite different. The increase in the curing temperature and the broadening of the exotherm for the blend (compared with that for PAA) indicate that the curing rate for the blend was less than that for PAA. This is important in terms of reaction control.

Although acetylene-containing resins have been researched for decades, the literature data do not allow a complete understanding of such unusual radical polymerization and many questions are still without answer.²⁴ It might be because of numerous ways in which polymerization can proceed and the fact

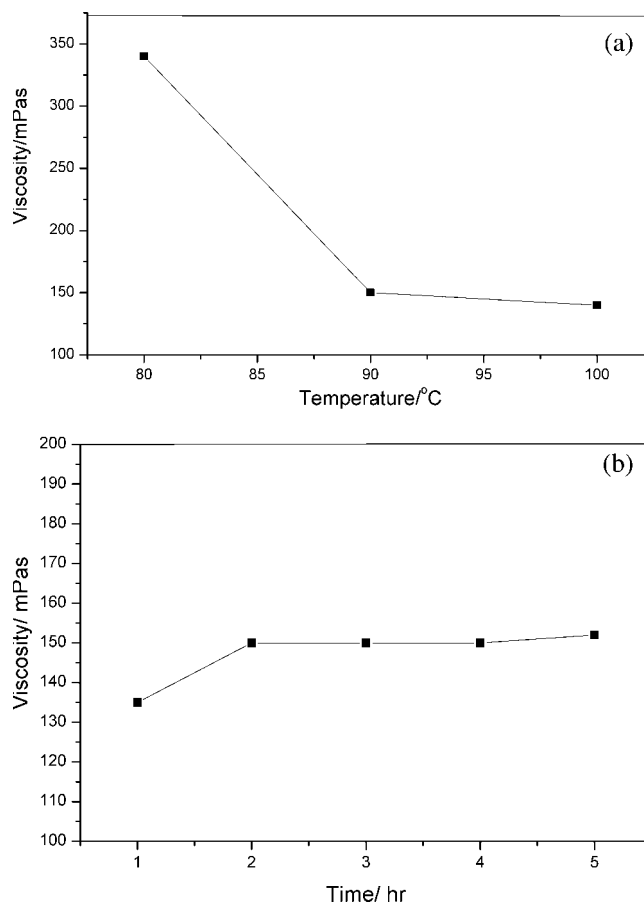


Figure 5 Rheology of PN-PAA (1 : 1) blend. (a) viscosity-temperature; (b) viscosity-time.

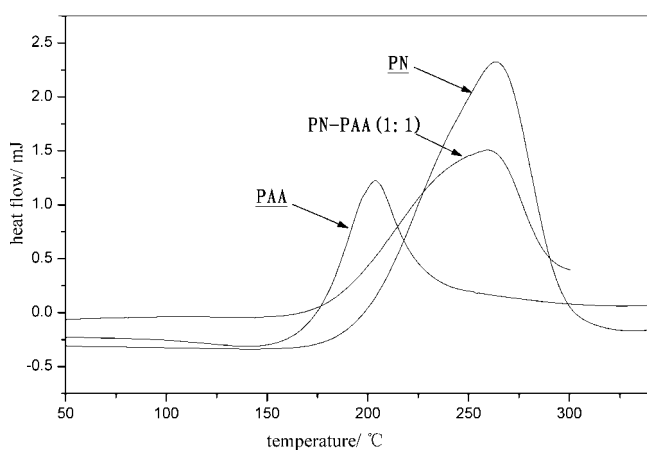


Figure 6 DSC profiles for thermal cure of PN-PAA (1 : 1) blend, PN, and PAA (scanning rate 10°C/min; N₂ purging rate 50 mL/min).

that few characterization techniques are available to study these complex thermoset structures.

Gel times of the blends increase with increasing PN content (PAA 5.3 min; PN-PAA (1 : 2) 20.37 min; PN-PAA (1 : 1) 50.28 min; and PN-PAA (2 : 1) 108.78 min). This composition dependency reveals that the proceeding of the crosslinking reactions of the blends can be regulated by change of PN ratio. In other words, the more the PN content is, the slower the curing reaction will be. Like PAA, there are no volatiles released for the PAA blends upon thermal cure. The above characteristics render the PAA blends a longer shelf life and more facile processing capability. In comparison with PAA resin, the blend resins possess highly improved processability suitable for low pressure processing techniques.

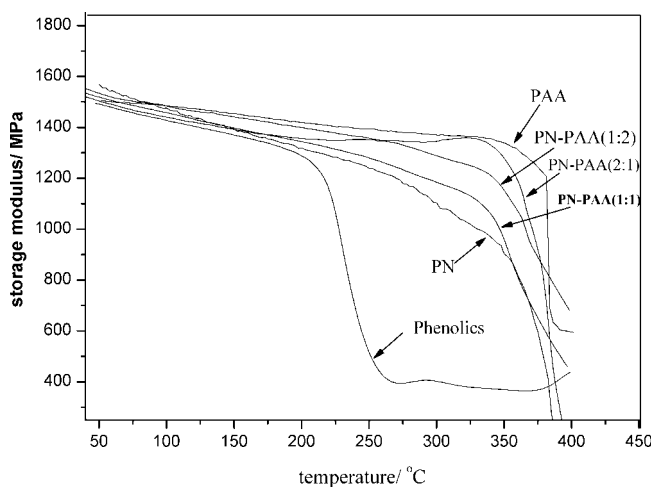


Figure 7 DMA profiles of the cured blends, PAA, PN, and phenolics (scanning rate 10°C/min; N₂ purging rate 50 mL/min; frequency 1 Hz).

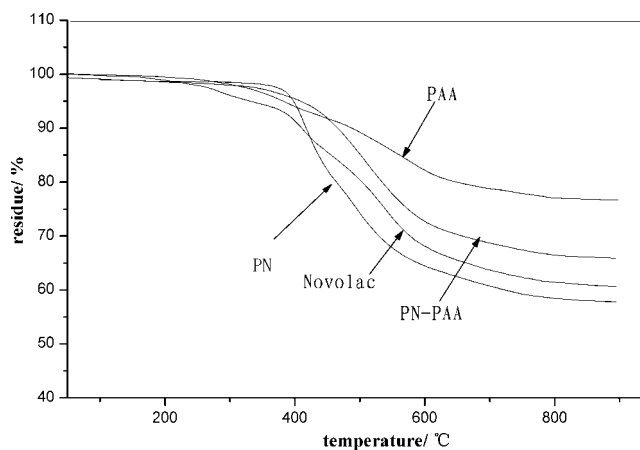


Figure 8 TGA profiles of the cured resins in N₂ (scanning rate 10°C/min; N₂ purging rate 30 mL/min).

Thermal stability of the blends

The cured blends are dark brown-red, transparent, and brittle solids. The thermal properties of the cured PN-PAA blends were evaluated by DMA and TGA techniques.^{25,26} DMA profiles of the cured blends are shown in Figure 7 together with those of the cured PAA, PN, and conventional phenolic resin. The cured blends exhibit glass transition temperatures higher than 360°C, much higher than that of conventional phenolic resin (T_g , ~ 230–280°C). The T_g of the blends are all lower than those of PAA and PN; the lowest T_g (~ 340°C) is that for the 1 : 1 blend. The results suggest that the blends can be utilized as a matrix for high temperature thermostructural composites.

Figure 8 shows TGA profiles of the cured PN-PAA (1 : 1), PN, PAA, and conventional phenolic resin in N₂ atmosphere. Before 420°C, the thermal resistance of PN-PAA (1 : 1) blend and PN are better than that of PAA, and much superior to that of conventional phenolics. This might be due to etherification of the

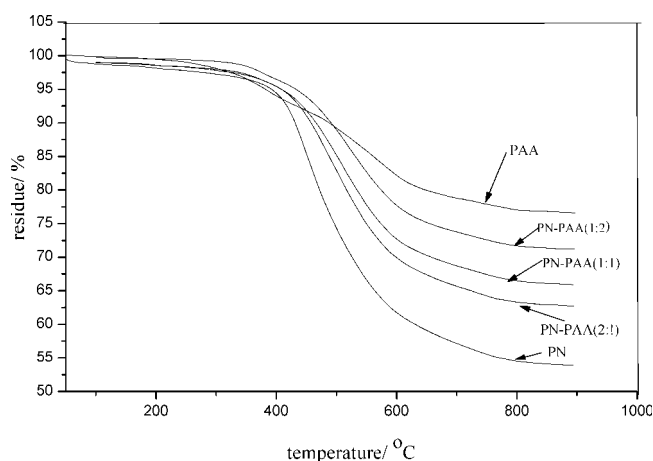


Figure 9 TGA profiles of the cured resins in N₂ (scanning rate 10°C/min; N₂ purging rate 50 mL/min).

TABLE I
Mechanical Properties of the Laminates

Matrix	Flexural strength (MPa)		Strength remaining ^a (%)	Flexural modulus (GPa)		Modulus remaining ^a (%)	ILSS (MPa)		ILSS remaining ^a (%)
	RT	350°C		RT	350°C		RT	350°C	
PAA	200	173	86.5	21.2	21.5	100	17.3	13	75
PN-PAA	309	228	74	25.2	23	91.3	22.5	17	75.6
PN	400			20.5			38.9		

^a Strength, modulus, and ILSS at 350°C.

phenols in PN, which improves the thermal stability of the resultant cured phenolic resin.²⁷ But, at higher temperatures, the pyrolysis rates increase in the order of PAA < (PN-PAA blend) < phenolics < PN, suggesting the importance of aromatic structure to thermal stability. Figure 9 shows the dependency of thermal decomposition on the composition of the blends. The initial decomposition temperatures (at about 410°C) were almost identical when the composition of the blends varied; and the anaerobic char residues decreased linearly with increase in PN content in the blend. This implies that thermogravimetry depends much on aromatic proportion. Propargyl groups can be cured into polyene and further three-dimensional networks,²⁸ but the thermal stability of these cured structures is inferior to that of the aromatic structures. Hence the content of PN in the blend should be controlled to be not higher than 50%. The anaerobic char residue of PN-PAA blend at 900°C was 67–68%, higher than that of the conventional phenolics (at 900°C, its anaerobic char residue is 58–60%).

The blends of PN and PAA are indeed a hopeful candidate, which can be applied as ablative materials.

Mechanical and thermal properties of the composites

The silica laminate composites were prepared to evaluate the blends as matrices for high temperature materials. From the standpoint of good processibility and thermal stability, the PN-PAA (1 : 1) blend was chosen as matrix for making laminates. The mechanical properties of laminates are listed in Table I, and those of PAA and PN laminates are also included for comparison. In comparison with PAA-matrix laminate, the blend-matrix composite exhibited marginally improved flexural strength and ILSS at both ambient temperature and high temperature, suggesting an enhanced interaction between fiber and matrix. The remaining percentages of strength and modulus for PAA-matrix material at high temperature are regarded as the highest so far; but those for the

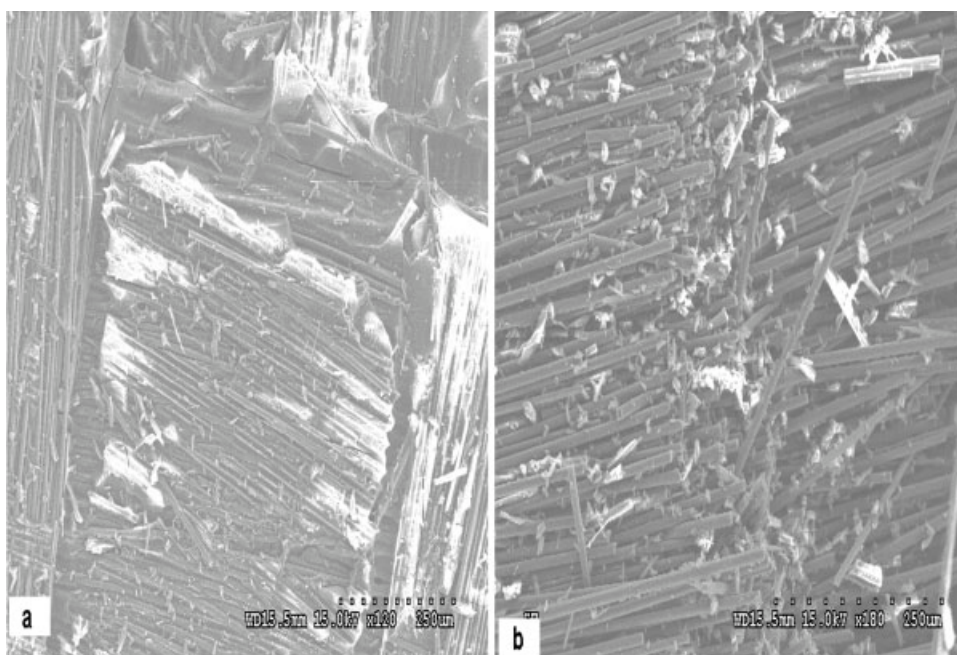


Figure 10 Typical SEM images for fractured surfaces of laminates: (a) PN-PAA matrix; (b) PAA matrix.

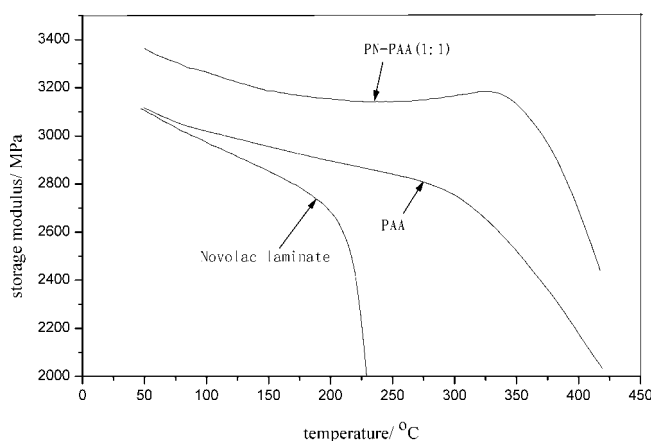


Figure 11 DMA profiles of silica cloth laminates (scanning rate 3°C/min; N₂ purging rate 50 mL/min; frequency 1 Hz).

blend-matrix material (the remaining percentage is above 74%) are comparable, and fairly better than those for conventional phenolics-matrix material (the remaining percentage is ~ 50%).¹

The ILSS values are representative of resin-fiber interaction at the interface in composites. It is crucial to transfer stress from matrices to fibers to ascertain effective reinforcement.²⁹ Furthermore, fine wetting of matrix resin to fibers at the interface is considered to be responsible for making composite materials with fewer voids, which are admirable in high temperature composite materials. The chemical interactions between silica fibers and polar PN molecules in the blend should be stronger than those between silica fibers and nonpolar PAA molecules, so the blend-matrix laminate exhibited higher ILSS than the PAA-matrix laminate. The morphology by SEM in Figure 10 conveyed this information.

Apparently, for PAA laminate, there were plenty of sheaths formed by fiber pulling out of matrix during mechanical test, and the surfaces of the pull-out fibers were bare, suggesting the poor adhesion between silica fibers and PAA matrix. But in the case of PN-PAA laminate, it could be found that many debris of the matrix were attached to the surfaces of the pull-out fibers.³⁰ The results revealed that the interfacial adhesion was improved markedly by blending PN to PAA. The ability of stress transfer from matrix to fibers mainly depends on ILSS, so this led to the improved flexural strength.

The DMA profile of the blend laminate is shown in Figure 11 together with those of PAA and novolac-type phenolic laminates.

Glass transition temperature (represented by the onset temperature of storage modulus when the material was oriented to mechanical applications) was around 350–370°C for the blend laminate. It is much higher than that of novolac-type phenolic laminate

(T_g , ~ 210–230°C). This makes the blends possible for an alternate matrix to conventional phenolics to prepare high temperature thermostructural materials.

CONCLUSIONS

A novel addition-curable PN resin was synthesized, and binary blends of PAA with PN were developed. Evidenced from the results of DSC (determination of T_g), phase appearance and electron microscopic observation, good miscibility between PN and PAA could be realized. The PAA-PN blends exhibited improved processing capability: suitable rheology to various process techniques, tempered curing velocity, and no evolution of volatile. The cured blends possessed high thermal stability by DMA and TGA techniques. The carbon residues of the blends showed a decreasing trend with increase in PN content. The blend having a PN content of 1/2 showed T_g above 350°C and the char residue above 66% at 900°C. When compared with pure PAA laminate, the PAA-PN blend matrix laminate exhibited improved mechanical properties at both ambient temperature and high temperature (at 350°C). The strength remaining percentage of the blend-matrix laminate was as high as ~ 74%. The blending greatly improved the comprehensive quality of PAA resin.

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