

ISSN 1996-3394

Asian Journal of
Materials
Science

Thermal, Mechanical, Morphological and Flame Retardance Properties of DABA Modified Novolac/CFRP Composites

¹M.P. Sham Aan, ¹M. Krishna, ¹H.N. Narasimha Murthy and ²S.K. Rai

¹Research and Development Department of Mechanical Engineering, R.V. College of Engineering, Bangalore-560 059, India

²Sir M.V.P.G. Centre, Department of Polymer Science, University of Mysore, Mandya-571402, India

Corresponding Author: M. Krishna, Research and Development Department of Mechanical Engineering, R.V. College of Engineering, Bangalore-560 059, India Tel: +91-80-28600535 Fax: +91-80-28602148

ABSTRACT

This study performed to investigate the effect of addition of 0, 0¹Diallyl Bisphenol A (DABA) on the thermal, mechanical, morphological and flame retardance behaviour of Novolac Phenolic/Carbon fibre composites. The miscibility of DABA and novolac phenolic resin was studied using DSC. Both modified and unmodified novolac phenolic resin were characterised for chemical structure using FTIR. TGA studies reveals that DABA modified novolac have better thermal stability. The results indicate that the appropriate content of DABA can significantly improve the mechanical properties such as the tensile strength, flexural strength, interlaminar shear strength and Impact strength of DABA modified novolac composites without compromising inherent flame retardant property. The 8 wt.% DABA modified novolac composites yielded more than 100% increase in impact strength compared to that of unmodified novolac composites. SEM studies of the tensile fractured specimens revealed that modification of novolac resulted in improved resin/fibre interfacial strength.

Key words: DABA, novolac phenolic resin, FTIR, carbon fibre, mechanical properties, SEM

INTRODUCTION

Phenolic resin has widely used in industry because of its good flame retardance, electrical insulation, dimensional stability and chemical resistance (Chiang, 2001; Goswami *et al.*, 2005). However, the poor wet-out between fiber and phenolic resin and the brittleness of phenolic resin are serious problems of the fiber-reinforced phenolic composite. All the mechanical properties of modified phenolic resin can be increased by incorporating flexible groups into the resin matrix (Wang *et al.*, 1999a). For example, either ester groups or other hydrogen-bonding functional groups are more flexible than is phenolic resin. Hence, modified phenolic resin, which will absorb more loads, can improve the brittleness of novolac-type phenolic resin (Ma *et al.*, 1998, 2001; Lee *et al.*, 1998; Wu *et al.*, 1997). Carbon fibers have been widely used as reinforcement in composites for thermal protection due to their superb dimensional stability at high temperatures, low density and a variety of outstanding physical and mechanical properties. The carbon fibre ratio (%) in the fabric has a significant effect on improving mechanical and physical properties of composite materials (Abd El-Hady and Abd El-Baky, 2011). In the production of carbon fiber-reinforced composites, the materials are typically preformed as prepregs for easy handling and processing (Park and Kang, 2002; Rimdusit *et al.*, 2009; Wang *et al.*, 2008;

Sulaiman *et al.*, 2008). Among carbon fibres both PAN based and Pitch based carbon fibres are used for particular applications (Babu *et al.*, 2006). Researchers tried to reduce brittleness of the phenolic resin through modifying/blending with different elastomers and other thermoplastic polymers. Novolac phenolic resin was modified with polyethylene oxide and improved flexural strength and ILSS of carbon/carbon composites (Hung *et al.*, 2002). Modification of the phenolic resin with p-Hydroxyphenylmaleimide/Acrylic ester copolymer and showed that the ester based copolymer have higher toughness than the phenolic resin (Matsumoto *et al.*, 1992). The phenolic resin modified with polyamide showed better bonding between fiber and matrix (Wang *et al.*, 1999b). Hydroxyl terminated polybutadiene using resole as compatibilizer improves the fracture toughness of the phenolic novolac resin (Nirmal *et al.*, 2006). The brittleness of the phenolic composites was reduced by reducing void content using ester based blocked polyurethane as toughening agent (Wu *et al.*, 1996). CFRPs can be used for strengthening concrete beams (Alzoubi and Zhenfliang, 2007; Alam and Jumaat, 2009).

The present study describes an attempt to improve toughness of the novolac phenolic resin by blending with DABA without compromising its inherent fire properties. Although many researchers have worked on novolac phenolic resin with many toughening agents to improve mechanical properties, no literature is available on the fire retarding properties of novolac phenolic composites toughened with DABA.

MATERIALS AND METHODS

Novolac phenolic resin (Fig. 1) was synthesised from phenol and formaldehyde by a reported procedure (Chiang and Ma, 2004) and was used as the matrix resin. DABA (Fig. 2) was supplied ABR organics, Hyderabad India. PAN based Carbon fabrics (204 g, plain weave, supplied by M/s CD Interglass Germany) were used as the reinforcement for the composites. The effect of the addition of DABA in different weight percentages on the viscosity of novolac phenolic resin was studied by Brookfield Viscometer (DV-II +PRO, USA). The miscibility between novolac phenolic resin and DABA was studied using Differential Scanning Calorimeter (DSC) calibrated with an indium standard. The DSC experiment conducted at a heating rate of $5^{\circ}\text{C min}^{-1}$ with nitrogen environment.

The chemical structure of the unmodified and modified novolac resin was studied using FTIR spectroscopy. The samples for FTIR analysis were mixed with KBr powder, pressed in to pellets and introduced into Perkin Elmer spectrum GXA Fourier transform infrared (FTIR) spectrophotometer at a resolution of 4 cm^{-1} in an optical range of $400\text{-}4000\text{ cm}^{-1}$.

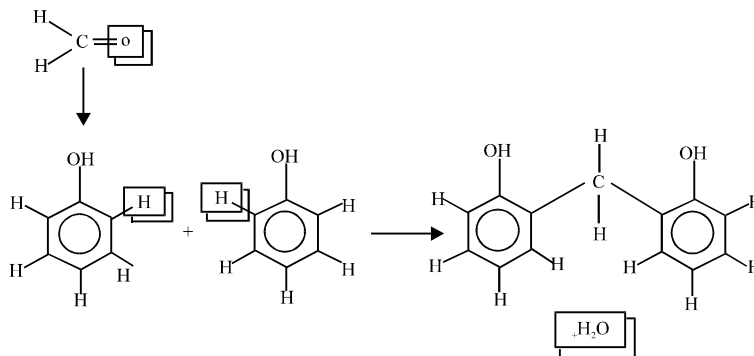


Fig. 1: Condensation reaction for the formation of phenol formaldehyde

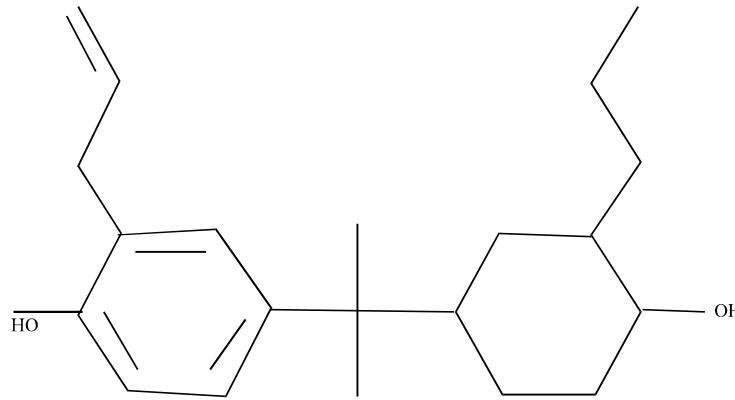


Fig. 2: Chemical structure of Di allyl Bisphenol A (DABA)

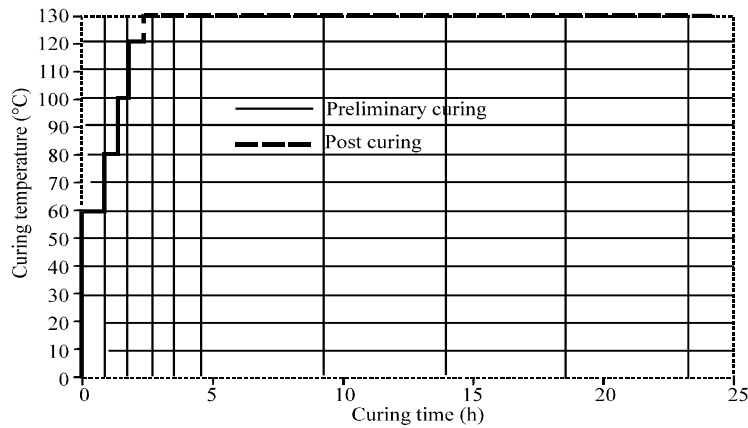


Fig. 3: Processing cycle of the novolac carbon fiber reinforced composites

Thermal degradation of the novolac resin and DABA modified novolac resin was examined with Du Pont 951, Thermo Gravimetric Analysis (TGA) instrument from room temperature to 800°C with a heating rate of 10°C min⁻¹ under nitrogen atmosphere. The measurements were conducted with 6-10 mg samples. Weight-loss/temperature curves were recorded.

The novolac phenolic resin with 10 wt.% hexamine catalyst was blended with 2 to 10 wt.% of Di allyl bisphenol A (DABA). This blend was used as a matrix to impregnate the carbon fiber (pre-pregs) using brushing impregnation technique and dried at room temperature for 24 h. Twenty plies of pre-pregs were stacked in a metal mold of dimensions 24×12×0.3 cm and cured at pressure of 4 MPa. The heating temperature profile of the die controlled by two heating plates along the compression direction is 60°C for first hour, 80°C for 30 min, 100°C for 30 min and 120°C for 30 min. After curing the samples were subjected to post curing at 130°C for 24 h (Fig. 3). But the processability of the composites becomes difficulty due to higher viscosity at higher percentage of DABA (>8 wt.%).

Void content of both the novolac phenolic composites and modified novolac phenolic composites with various DABA contents were studied as per ASTM D 2734.

Novolac phenolic/carbon fiber and modified novolac phenolic/carbon fiber composites were tested for ultimate tensile strength as per ASTM D-3039 standard using universal testing machine (M/s Kalpak, Pune) with a cross head speed of 5 mm min^{-1} . Five samples were tested and average values was reported.

The flexural strength of the both unmodified and modified novolac phenolic composites was determined using the three-point bend method as per ASTM-D790 standard. Five specimens with span length of 100 mm and cross-head speed of 2 mm min^{-1} were tested and average values were reported.

The Inter Laminar Shear Strength (ILSS) tests were conducted using three-point bend technique according to ASTM D-2344 standards with cross head speed of 1 mm per minute. Five samples were tested and average value was reported.

The Izod impact strength of both unmodified and modified composites was measured as per ASTM D-256, using Izod impact testing machine. Fracture surfaces of the tensile specimens were studied using scanning electron microscope to know interfacial adhesion between matrix and reinforcement. The morphology of the tensile fractured composites specimens were studied using JEOL JSM840A-(Japan) Scanning Electron Microscope (SEM).

The L.O.I is defined as the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion. The L.O.I. test was conducted according to the ASTM D 2836 Oxygen Index Method using a test specimen bar 7-15 cm long, 6.5 mm wide and 3 mm thick. The sample bars were suspended vertically and ignited using OR by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was increased if the specimen was extinguished before burning away for 3 min or 5 cm. The oxygen content was adjusted until the limiting concentration was determined.

The UL-94 vertical test was performed according to the ASTM D 3801 testing procedure with a test specimen bar 127 mm long, 12.7 mm wide and about 3 mm thick. Five sample bars were suspended vertically over surgical cotton and ignited by a Bunsen burner. A flame was applied twice to the lower end of the specimen for 10 sec. The specimen was assigned to the class UL-94 V-0 when each after-flame time did not exceed 10 sec and the sum of the after-flame times for five samples did not exceed 50 sec. Assignment to class UL-94 V-0 also required that the flaming drops could not ignite the surgical cotton below the specimen. Assignment to class UL-94 V-1 required that each after-flame time did not exceed 30 sec and the sum of the after-flame times for the five samples did not exceed 250 sec. Assignment to class UL94 V-1 also required that flaming drops did not ignite the surgical cotton below the specimen. If the flaming drops ignited the surgical cotton below the specimen, then the sample was assigned to class UL-94 V-2.

RESULTS AND DISCUSSION

Viscosity studies: Figure 4 shows the viscosity change with the different weight% loading of DABA. It was found that with the increase of the percentage content of DABA, the viscosity of the total resin system increased and at 10% weight of DABA the viscosity becomes very high beyond which the processability of the system decreased remarkably. Hence this study is constrained within a maximum of 10% weight of DABA.

Miscibility studies: Figure 5 shows the second run DSC curves for novolac resin (curve-a) and modified novolac resin with 2 wt.% (curve-b), 4 wt.% (curve-c) and 10 wt.% (curve-d) of DABA. The miscibility was mainly ascertained on the bases of the occurrence of a single Tg behavior observed

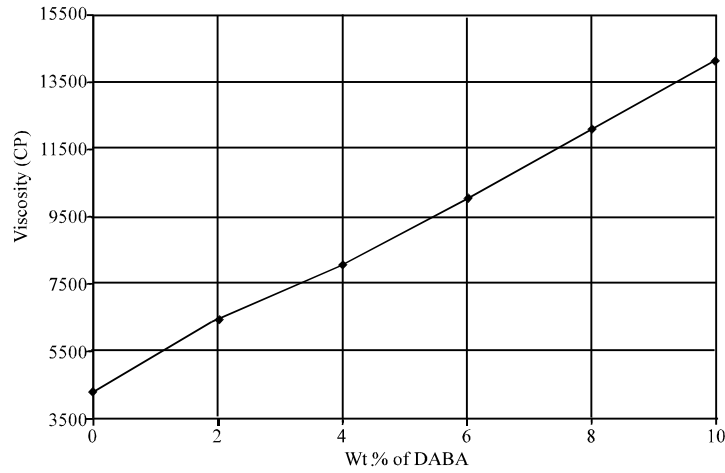


Fig. 4: Viscosity of novolac resin blended with different wt.% of DABA

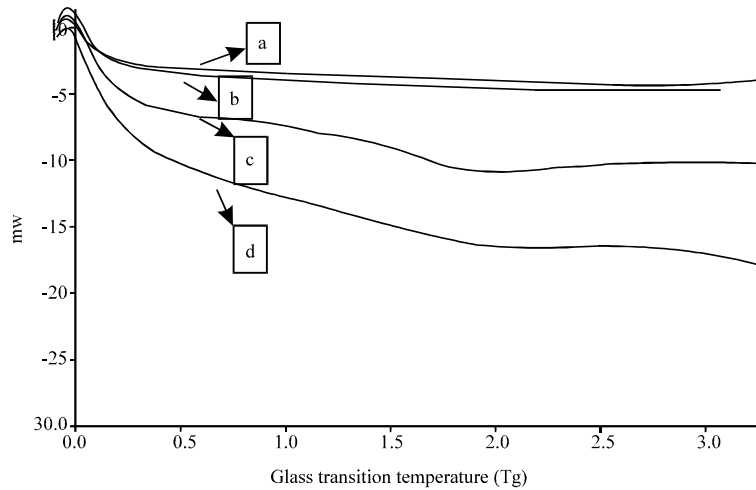


Fig. 5: DSC graph of Novolac blended with different wt.% of DABA (a) Pure Novolac, (b) 2 wt.% (c), 8 wt.% and (d) 10 wt.%

throughout the whole blend range at various compositions of phenolic blends, suggesting that the novolac/DABA blend system in this study is directly miscible which is in concurrence with elsewhere studies (Wen-Bin *et al.*, 2006).

FTIR studies: The interaction between novolac and DABA was corroborated by FT-IR spectroscopy. The FT-IR spectra of unmodified novolac and Cured modified novolac with DABA are presented in Fig. 6. Unmodified novolac shows a band at 3500 cm^{-1} which is assigned to the non associated free hydroxyl groups. The flexible allyl group chain intersects into the free volume of a phenolic matrix and provides more opportunity to form intermolecular hydrogen bonding and also increases the average strength of the hydrogen bonding in this blend system. Peak broadening can be observed in modified novolac which indicates hydrogen bonding implies better interaction between the two components. This will lead to the increase in mechanical properties of the composites.

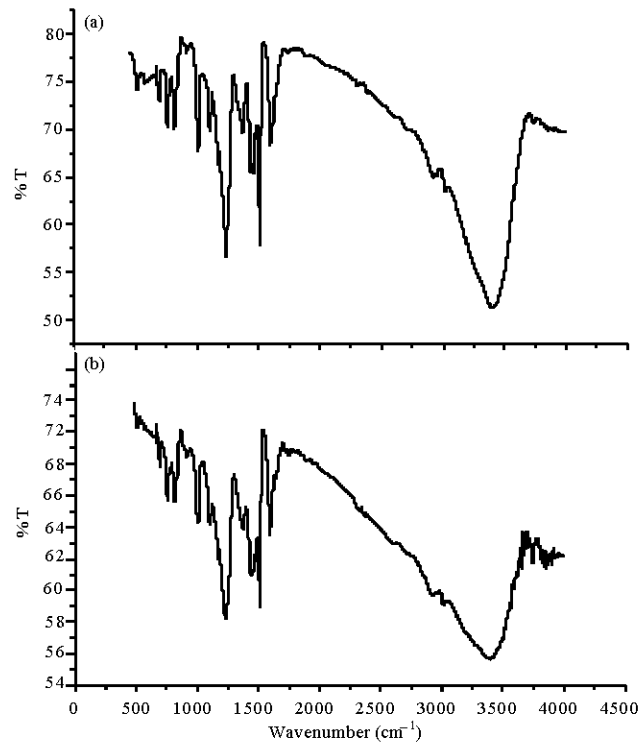


Fig. 6: FTIR Spectrum of (a) Unmodified Novolac and (b) Modified cured Novolac with 8% DABA

TGA studies: Figure 7 depicts TGA curves of the neat novolac resin and DABA modified novolac resin. The TGA curves range from room temperature to 800°C in an atmosphere of N₂. The char yields of the modified novolac increased with the amount of DABA. Increasing the char forming reduces the production of combustible gases, decreases the exothermicity during pyrolysis reactions and inhibits the thermal conductivity of the burning materials. The decomposition temperature of the DABA modified novolac resin is more than neat novolac resin indicating that modified novolac resin has good thermal stability.

Mechanical properties (UTS, FS, ILSS, Impact Strength): Figure 8-11 shows the UTS, FS, ILSS and Impact strength respectively for both unpostcured and postcured novolac phenolic composites modified with different wt.% of DABA. The mechanical properties attained the greatest values at 8 wt.% DABA addition in both post cured and unpostcured composites. UTS, FS, ILSS and impact strength increased by 18, 17, 47 and >100%, respectively in postcured specimens at 8 wt.% DABA addition compared to that of unmodified novolac composites. It is well known that voids have detrimental effects on the strength of the composite laminates (Stone and Clark, 1975). The improvements are attributed to the decrease in voids (Fig. 12) which act as defect sites and initiate cracks leading to premature failure. Chain modifier DABA improved the matrix/fibre compatibility. It contains flexible allyl group which reduces the cross linking density. The softening of the matrix helps to absorb fracture energy. The improvements in mechanical properties were lower in case of unpostcured composites because of incomplete reaction. The addition of more than 8 wt.% DABA increased the viscosity of the phenolic resin leading to processing difficulties.

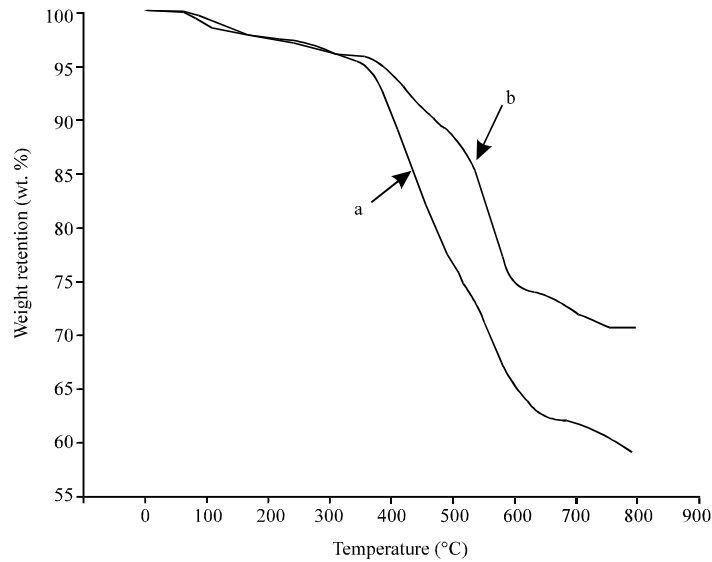


Fig. 7: TGA curves of (a) novolac resin and (b) DABA modified novolac resin

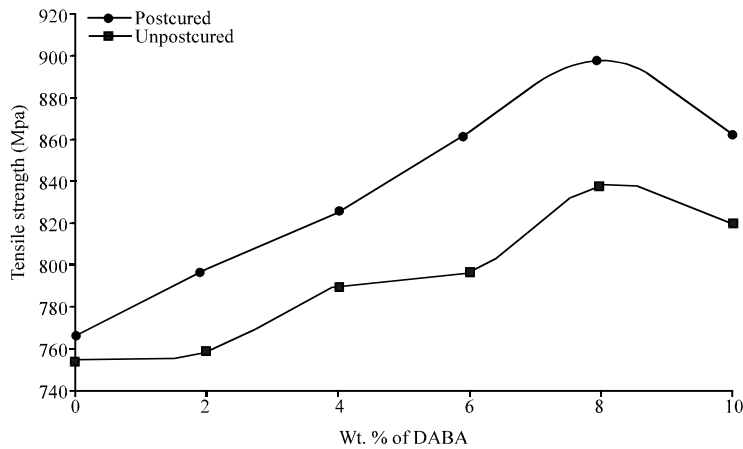


Fig. 8: Effect of wt.% of DABA on Tensile Strength of carbon fibre reinforced novolac composites

Morphology of the composite: Fractured morphology indicates fibre bundle brittle fracture and pull out for the symmetrical ply arrangements (Bang *et al.*, 2007). Figure 13a-f show the SEM micrographs of tensile fractured specimens of CFRPs based on novolac phenolics modified with 0 to 10 wt.% in steps of 2 wt.% of DABA, respectively. The micrographs showed that the fibre bundles were evenly distributed without fibre breakage in the unmodified specimens. The weak fibre/matrix adhesion leads to fibre pull out as the dominant failure mechanism in them. The fibre/matrix strength increased with increase in % DABA addition up to 8 wt.% which is evident from the occurrence of greater degree of fibre breakage in these specimens. Further increase in loading of DABA modified specimens showed lesser degree of fibre breakage (Fig. 13f), indicative of lesser interfacial strength. The flexible allyl group of DABA interacts with the hydroxyl group of phenolic and increases the mobility of the phenolic resin along with the wet-out of the matrix and the carbon fibre.

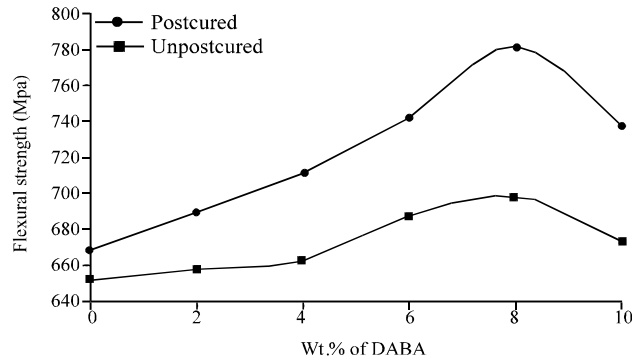


Fig. 9: Effect of wt. % of DABA on flexural strength of carbon fibre reinforced novolac composites

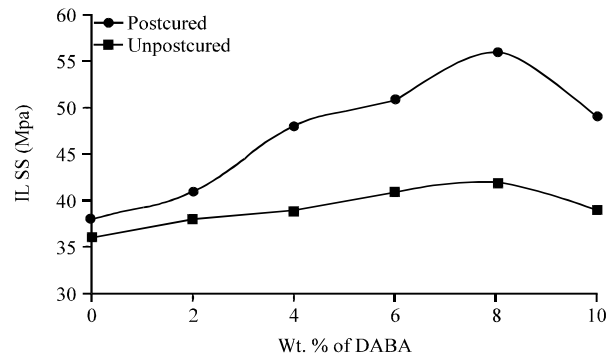


Fig. 10: Effect of wt.% of DABA on ILSS of carbon fibre reinforced novolac composites

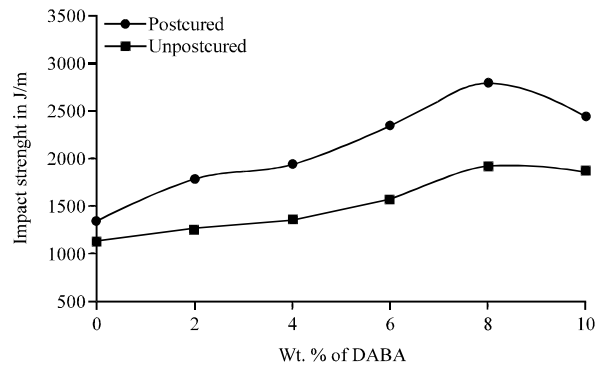


Fig. 11: Effect of wt.% of DABA on impact strength of carbon fibre reinforced novolac composites

Fractured morphology also indicates fibre bundle brittle fracture and pull out for the symmetrical ply arrangements. Whereas unmodified and 2 wt.% DABA modified phenolic composites showed the presence of cracks, it was absent in composites with higher percentage of DABA indicating greater toughness.

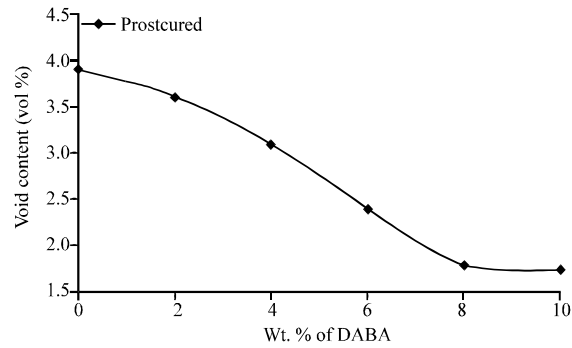


Fig. 12: Effect of wt.% of DABA on void content of carbon fibre reinforced novolac composites

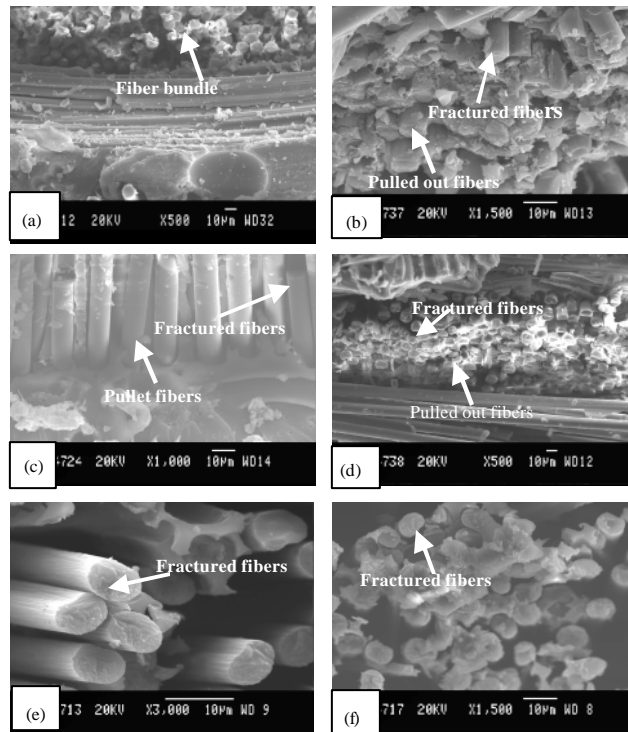


Fig. 13: SEM photographs of carbon fibre reinforced novolac resin composites modified with various DABA contents (a) 0 wt.%, (b) 2 wt.%, (c) 4 wt.%, (d) 6 wt.%, (e) 8 wt.% and (f) 10 wt.%

Flame retardance: The percentage of oxygen in the O_2 and N_2 mixture, just sufficient to sustain the flame, is taken as the LOI. The LOI values can be used to estimate the flame retardancy of materials. The LOI value and flame retardance of unmodified and modified novolac phenolic carbon fibre reinforced composites are given in Table 1. Which shows an extremely high LOI value is >55

Table 1: The flame retardance of carbon fibre reinforced modified novolac phenolic composites

DABA Content(wt.%)	0	2	4	6	8	10
UL-94	V-0	V-0	V-0	V-0	V-0	V-0
Limited Oxygen Index (LOI)	> 55	> 55	> 55	> 55	> 55	> 55

and flame retardance values of UL-94, V-0. The both standard values are maintained in all percentage DABA added. There was no compromising in the parent materials flame retardance property after modification with improved mechanical properties.

CONCLUSIONS

The modification of novolac phenolic resin with DABA not only improved the mechanical properties but also it retained its inherent flame retardance properties. The DSC study reveals that phenolic/DABA blend is a completely miscible system. DABA is a good reagent for toughening the phenolic resin. Thermal resistance of novolacs improved by the incorporation of DABA. All mechanical properties showed that 8 wt.% of DABA/novolac phenolic resin blends have the maximum values. The post cured composites showed higher mechanical values such as tensile, flexural, ILSS and impact strength than that of uncured composites due to complete curing of the composites. The flame retardance to 10 wt.% DABA in modified novolac phenolic carbon fibre reinforced composites shows values of UL-94 at V-0 with the LOI at more than 55, showing excellent fire resistant properties. The fracture surface study showed that better adhesion between matrix and the reinforcement hence the mechanical properties enhanced.

REFERENCES

- Abd El-Hady, R.A.M. and R.A.A. Abd El-Baky, 2011. Enhancing the functional properties of sportswear fabric based carbon fiber. *Asian J. Textile*, 1: 14-26.
- Alam, M.A. and M.Z. Jumaat, 2009. Eliminating premature end peeling of flexurally strengthened reinforced concrete beams. *J. Applied Sci.*, 9: 1106-1113.
- Alzoubi, F. and L. Zhengliang, 2007. Overview shear strengthening of RC beams with externally bonded FRP composites. *J. Applied Sci.*, 7: 1093-1106.
- Babu, N.S., S.B. Tiwari and B. Nageswara Rao, 2006. Structural and morphological features of graphitised carbon fibres. *Trends Applied Sci. Res.*, 1: 204-213.
- Beng, Y.K., M.N. Dalimin and M.A. Faizal, 2007. Mode-I toughness and curing pressure characteristic of symmetrical lay-up of plain-weave woven GFRP composites. *J. Applied Sci.*, 7: 2174-2182.
- Chiang, C.L., 2001. Thermal mechanical and morphological properties of Novolac- Type phenolic resin blended with Fullernol Polyurethane and Linear poly urethane. *Comp. Part B*, 36: 2436-2443.
- Chiang, C.L. and C.C.M. Ma, 2004. Synthesis, characterization, thermal properties and flame retardance of novel phenolic resin/silica nanocomposites. *Polym. Degradation Stability*, 83: 207-214.
- Goswami, S., S. Nad and D. Chakrabarty, 2005. Modification of novolac resin by interpenetrating network formation with poly (butyl acrylate). *J. Applied Polym. Sci.*, 97: 2407-2417.
- Hung, A.Y.C., F.Y. Wang, S.R. Yeh, W.J. Chen and C.C.M. Ma, 2002. Carbon/carbon composites derived from (Polyethylene oxide)-modified novolac type phenolic resin: Microstructure, physical and morphological properties. *J. Applied Polym. Sci.*, 84: 1609-1619.

- Lee, C.T., H.D. Wu, P. Chu and C.C.M. Ma, 1998. Strength of hydrogen bonding in the novolak-type phenolic resin blends. *J. Polym. Sci. Part B Polym. Phys.*, 36: 1721-1728.
- Ma, C.C.M., C.T. Lee and H.D. Wu, 1998. Mechanical properties, thermal stability, and flame retardance of pultruded fiber-reinforced poly(ethylene oxide)-toughened novolak-type phenolic resin. *J. Applied Polym. Sci.*, 68: 1129-1136.
- Ma, C.C.M., F.Y. Wang, H.J. Lin, S.H. Wu and J.C. Yang, 2001. Mechanical properties, thermal stability, and flame retardance of novolac type phenolic resin blended with poly(dimethylsiloxane adipamide). *J. Applied. Polym. Sci.*, 79: 631-637.
- Matsumoto, A., K. Hasegawa, A. Fukuda and K. Otsuki, 1992. Study on modified phenolic resin. III. Modification with p-hydroxyphenylmaleimide/acrylic ester copolymer. *J. Applied Polym. Sci.*, 44: 1547-1556.
- Nirmal, C., S.N. Maithi, T. Padmavathi, A. Vanaja and R.M.V.G.K. Rao, 2006. Studies on hydroxyl terminated polybutadiene toughened phenolic resin. *High Performance Polym.*, 18: 57-69.
- Park, J.K. and T.J. Kang, 2002. Thermal and ablative properties of low temperature carbonfiber-phenol formaldehyde resin composites. *Carbon*, 40: 2125-2134.
- Rimdusit, S., P. Jongvisuttisun, C. Jubsilp and W. Tanthapanichakoon, 2009. Highly processable ternary systems based on benzoxazine, epoxy and phenolic resins for carbon fiber composite processing. *J. Applied Polym. Sci.*, 111: 1225-1234.
- Stone, D.E. and B. Clark, 1975. Ultrasonic attenuation as a measure of void content in carbon fibre reinforced plastics. *Non Destructive Testing*, 8: 137-145.
- Sulaiman, S., R. Yunus, N.A. Ibrahim and F. Rezaei, 2008. Effect of hardener on mechanical properties of carbon fibre reinforced phenolic resin composites. *J. Eng. Sci. Technol.*, 3: 79-86.
- Wang, F.Y., C.C.M. Ma and W.J. Wu, 1999a. Mechanical properties, morphology, and flame retardance of glass fibre-reinforced polyamide-toughened novolac type phenolic Resin. *J. Applied Polym. Sci.*, 73: 881-887.
- Wang, F.Y., C.C.M. Ma and H.D. Wu, 1999b. Hydrogen bonding in polyamide toughened novolac type phenolic resin. *J. Applied Polym. Sci.*, 74: 2283-2289.
- Wang, Z.L., Y.C. Li, T. Zhang, Z.H. Wang and X.J. Wang, 2008. A study on mechanical properties of carbon/phenolic composites. *Mechanics Mater.*, 40: 418-426.
- Wen-Bin, L., T. Shih-Huang, L. Wei-Chi and Y. Ling-Yueh, 2006. Studies on blends of binary crystalline polymers: Miscibility and crystallization behaviour in PBT/PAr (I27-T73). *Polymer*, 47: 8380-8388.
- Wu, H.D., M.S. Lee, Y.D. Wu, Y.F. Su and C.C.M. Ma, 1996. Pultruded fiber-reinforced polyurethane-toughened phenolic resin. II. Mechanical properties, thermal properties and flame resistance. *J. Applied Polym. Sci.*, 62: 227-234.
- Wu, H.D., C.C.M. Ma and J.M. Lim, 1997. Processability and properties of phenoxy resin toughened phenolic resin composites. *J. Applied Polym. Sci.*, 63: 911-917.