

# Influence of Poly (vinyl butyral) Modification on the Mechanical and Thermal Properties of Kevlar Fiber Reinforced Novolac epoxy/multiwalled carbon nanotube nanocomposites

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## ABSTRACT

*The effect of poly (vinyl butyral) and acid functionalized multiwalled carbon nanotubes (f-MWCNT) on the thermal and mechanical performance of Kevlar fiber reinforced novolac epoxy nanocomposites was investigated and presented in this paper. Nanocomposite containing 1.5 wt. % poly (vinyl butyral) and 0.5 wt. % f-MWCNT exhibited best thermal and mechanical properties (except flexural strength) among all the nanocomposites reported here. It showed ~5%, 27% and 126 % improvement in tensile strength, young's modulus and impact strength respectively as compared to the neat novolac epoxy Kevlar composite. Nanocomposite containing 0.5 wt. % f- MWCNT and 2 wt. % poly (vinyl butyral) showed best flexural strength and modulus among all the nanocomposites with increment of about 91% and 56 %.*

KEYWORDS: *Kevlar fiber, f-MWCNT, PVB, thermal properties, mechanical properties.*

## INTRODUCTION

Polymer matrix composites (PMCs) have become an attractive area of material's research due to their light weight, high stiffness, corrosion resistance, high thermal stability, easy processing and many other desirable properties which make them suitable for

industrial and defence applications<sup>[1-2]</sup>. PMCs are basically made up of two or more constituent materials having different physical and chemical properties. These constituent materials are broadly divided in two categories: matrix and reinforcement. Matrix acts as the load carrying part of fiber reinforced (FR) composites for the reinforcement. Matrix may be thermoplastic or

thermosetting resins. Among thermoplastic resins polyvinyl acetals, polyurethanes, polyesters etc. are common matrix materials. In case of thermosetting resins phenolic and epoxy resins are the most common matrices used in the high performance FR composites. Reinforcing materials may be of two types particulate and fabric reinforcement. Many natural and synthetic fibers are used as reinforcement in FR composites. Some examples of natural fibers are: flax, jute, hemp, sisal, bamboo, cotton etc<sup>[3-4]</sup>. Among synthetic fibers glass, carbon, aramid and ultra-high molecular weight polyethylene (UHMWPE) fibers are commonly used in fabrication of FR composites<sup>[5-7]</sup>.

In literature, many studies have been reported using natural and synthetic fibers and evaluated their thermal, mechanical properties<sup>[8-26]</sup>. For structural and defence applications Kevlar fibre based composites are superior to glass and carbon fibre based composites due to their higher flexibility and optimum cost. Many researchers have studied the thermal and mechanical properties of Kevlar/epoxy composites and compared their properties with metal (steel) and variety of natural and synthetic fiber based composites. Warbhe *et al.*, have fabricated the jute and Kevlar reinforced composites and studied the effect of incorporation of Kevlar fiber on the mechanical properties of jute composites. They found that Kevlar fiber significantly improved the tensile, flexural and impact strength of composites. Weight reduction in Kevlar fiber based composite was also achieved<sup>[27]</sup>. Ananda Rao *et al.*, have compared the mechanical properties of Kevlar fiber with mild steel. They reported the noteworthy increase in tensile

strength of Kevlar/epoxy composites as compared to steel. The tensile strength of Kevlar composites was found to be 403 MPa whereas for steel it was 210 MPa. Compression load and bending load were also increased for Kevlar composites as compared to steel<sup>[28]</sup>. But Kevlar fibres show less adhesion with epoxy resin as compared to glass and carbon fibres. Therefore, we have blended a very small amount of PVB with epoxy resin in order to improve the fibre matrix adhesion as PVB possesses three different functional groups (acetate, hydroxyl and acetal group) and good adhesion properties with different materials. Besides, increasing the adhesion as well as flexibility PVB simultaneously decreases the thermal as well as mechanical stability of the composites. Nowadays, use of nanofillers is very popular for enhancing the thermal as well as mechanical strength of composites. Very small amount of nanofillers (inorganic or organic) are effective in increasing thermal and mechanical properties of composites. Among nanofillers, carbon based (carbon nanotubes, graphene, fullerenes, etc.) nanofillers are very much used for high performance composite applications. Some researchers have done the functionalization of nanofillers in order to improve the interfacial interaction and dispersion of nanofillers within the matrix. Simcha *et al.*, have studied the effect of titania coated MWCNT on the thermo-mechanical properties of epoxy composites. They reported the 10 and 30% increase in glass transition temperature and storage modulus by incorporating 0.3-0.5 wt. % surface treated MWCNT<sup>[29]</sup>. Mulan Mu *et al.*, and Inam *et al.*, have separately investigated the effect of MWCNT length on mechanical properties of PMMA/epoxy matrix nanocomposites. They

found that tensile stress and strain to failure increased with increasing MWCNT length<sup>[30], [31]</sup>. Jagtap *et al.*, have found the improved tensile and dynamic mechanical properties of epoxy nanocomposites by incorporating 6-amino hexanoic acid functionalized CNT<sup>[32]</sup>.

Therefore, in the present research, we have fabricated the Kevlar fiber reinforced composites using PVB/f-MWCNT/novolac epoxy as a matrix material and reported the effect of f-MWCNT/PVB modified resin on thermal and mechanical properties of Kevlar fibre reinforced composites. In this experiment, f-MWCNTs are used to improve the interfacial interaction between the novolac epoxy and Kevlar fibres as small amount of nanofillers radically improved the thermal, mechanical properties of final nanocomposites due to their unique structure<sup>[29]</sup>. Functionalization of nanofillers has been done to improve the dispersion in the novolac epoxy matrix.

## EXPERIMENTAL

### Materials

Kevlar fabric 280 gsm with thickness of 0.25mm was supplied by Dupont, USA. Curing agent 4,4 Diaminodiphenyl methane (DDM) was purchased from E. Merck (India) Limited, Mumbai. MWCNT (length 5-9  $\mu\text{m}$  and diameter 110-170 nm) was kindly supplied by

Sigma Aldrich. Methyl ethyl ketone was purchased from Samir Tech.–Chem. Pvt. Ltd. Polyvinyl butyral used in study was received from Synpol Pvt. Ltd. Ahmedabad, India.

### Fabrication of Kevlar fiber reinforced nanocomposites

Experimental and characterization details of synthesis of novolac epoxy resin and acid functionalization of MWCNT were reported in our previous study<sup>[33]</sup>. Kevlar fiber reinforced novolac epoxy nanocomposites were fabricated by using modified novolac epoxy resin as a matrix material. Modification of novolac epoxy resin was carried out by blending the resin with constant f-MWCNT (0.5 wt. % of novolac epoxy) and varying PVB (1.0, 1.5 and 2.0 wt % of novolac epoxy) content. Fiber to PVB and f-MWCNT modified novolac epoxy resin (please see Table 1 for details of composition) ratio was taken as 75:25. Kevlar fibers are hygroscopic in nature therefore, before fabrication process fibers were kept in vacuum oven at 50°C for 4-5 hours. All the nanocomposites were fabricated by hand layup technique. Initially, calculated amount of novolac epoxy resin was taken in a beaker and then PVB solution made in methyl ethyl ketone (MEK) and sonicated f-MWCNT both were added in the novolac epoxy resin and

TABLE 1. Compositions of PVB and f-MWCNT modified novolac epoxy resin for fabrication of nanocomposites with Kevlar Fabrics (12 layers)

Sample code	Novolac epoxy (wt %)	PVB (wt %)	f-MWCNT (wt %)
<b>Composite A</b>	100	—	—
<b>Composite B</b>	98.5	1.0	0.5
<b>Composite C</b>	98.0	1.5	0.5
<b>Composite D</b>	97.5	2.0	0.5

homogenized for half an hour. Afterwards, in order to degas, the mixture was kept in vacuum oven for 15-20 minutes. Finally, optimum amount of hardener (30 wt. %, DDM) was added in the resin mixture and stirred well with the help of mechanical stirrer for 30 minutes. The modified novolac epoxy resin was applied on fabric plies one by one with the help of hand brush. After coating, 12 layers of fabric plies have been stacked one above the other. The fabricated nanocomposites were cured by initially placed in preheated compression molding press at 80°C for 1 hour at atmospheric pressure. Then, temperature was increased to 120°C with 5 tons of pressure for half an hour, followed by 160°C temperature with 10 tons of pressure for half an hour, and finally temperature was increased to 180°C for one hour with same pressure. Thereafter, nanocomposite was kept overnight in compression molding press under pressure at room temperature. To compare the properties of nanocomposites neat novolac epoxy based Kevlar fiber reinforced composite was also fabricated under similar experimental conditions.

### Characterization

#### Mechanical Characterization

Mechanical properties *viz.* tensile and flexural strength and modulus were investigated in INSTRON Universal Testing Machine (Model no. 3382) as per test method ASTM D-3039 and ASTM D-790. Izod impact strength was determined in Tinius Olsen impact testing machine according to ASTM D-256. For each nanocomposite at least five specimens were tested and average of these values was reported as the experimental result.

#### Thermal Analysis

Thermal stability of resulting nanocomposites was investigated in thermogravimetric analyzer (Q200, TA

instrument) by heating the sample from ambient to 800°C at the rate of 10°C/min under nitrogen atmosphere.

## RESULTS & DISCUSSION

### Mechanical properties

#### *Tensile properties*

Tensile properties of the Kevlar FR nanocomposites are presented in Figure 1. It is observed that 'Composite C' exhibited best tensile strength and Young's modulus among all the nanocomposites reported here. 'Composite C' showed ~ 5% and 27 % improvement in tensile strength and Young's modulus than the neat novolac epoxy based Kevlar composite. Elongation at break of all the nanocomposites was reduced as compared to neat novolac epoxy based Kevlar composite. In literature enormous work has been done on f-MWCNT based novolac epoxy nanocomposites and their thermal, mechanical properties have been studied<sup>[34]</sup>. They showed that mechanical properties of nanocomposites were dependent on dispersion of the f-MWCNT in novolac epoxy matrix and interfacial interaction between the nanofillers and polymeric matrix. In our study, novolac epoxy resin has been modified by PVB and f-MWCNTs. Therefore, the properties of resulting nanocomposites are governed by many factors like dispersion of f-MWCNT, distribution of PVB in novolac epoxy matrix, interaction of PVB and f-MWCNT with novolac epoxy matrix and interaction of PVB with f-MWCNT. All such interactions may be responsible for final mechanical properties of nanocomposites. 'Composite B' showed lower tensile strength than neat novolac epoxy based Kevlar composite. Reduced tensile strength of 'Composite B' may be due to the agglomeration

of f-MWCNT in the PVB matrix and in homogeneous dispersion of PVB in novolac epoxy matrix at such a low loading. On increasing the amount of PVB in 'Composite C' (1.5 wt % PVB) both the tensile strength and young's modulus are improved from the neat novolac epoxy based Kevlar composite. This is attributed to the better interfacial interaction between nanofiller and novolac epoxy matrix as well as homogenous dispersion of PVB in novolac epoxy phase.

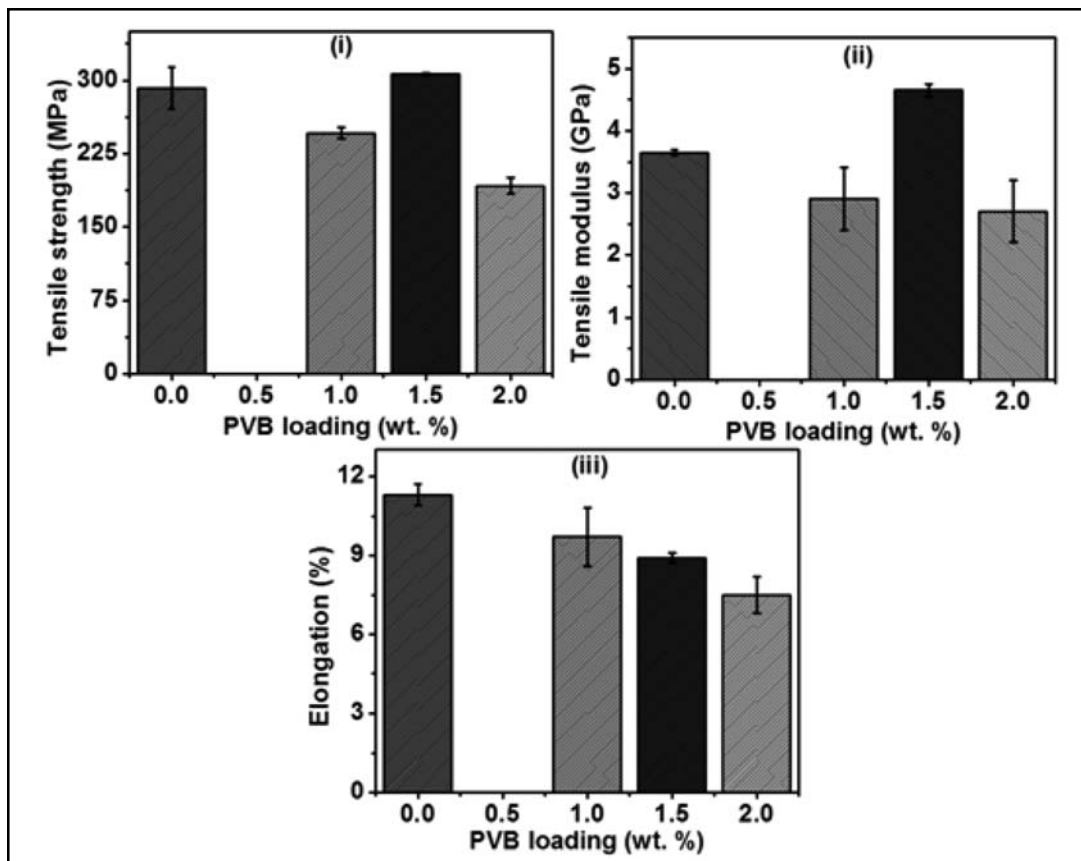


Fig. 1. (i) Tensile strength, (ii) tensile modulus and (iii) elongation of nanocomposites.

As a result of better interfacial interaction, matrix successfully transfers stresses to the fibers which leads to increased tensile strength of the nanocomposites as compared to neat novolac epoxy based Kevlar composite. On further increasing the amount of PVB in 'Composite D' (2 wt. % PVB) tensile strength and Young's modulus both are reduced. This is due to the presence of low strength and low modulus PVB which lowers the cross-link

density of novolac epoxy resin and f-MWCNT fails to overcome the decrement in tensile properties at 2 wt. % PVB content. PVB being a thermoplastic polymer with long aliphatic carbon chain, bonding of PVB with novolac epoxy resin introduces flexibility (functional group of novolac epoxy resin bonded with PVB instead of hardener) and therefore reduces cross linking density<sup>[35]</sup>. The reason for reduced elongation at break of all nanocomposites as compared to neat novolac epoxy based Kevlar composite is restriction imparted by f-MWCNT to the segmental motion of novolac epoxy resin.

#### *Flexural properties*

Flexural properties of Kevlar FR nanocomposites are represented in Figure 2. All the nanocomposites showed superior flexural strength and modulus than neat novolac epoxy based Kevlar composite. Flexural strength and modulus of nanocomposites are increased as amount of PVB was increased (f-MWCNT remains constant (0.5 wt. %) in all the nanocomposites). 'Composite D' showed

highest flexural strength and modulus among all the compositions. It exhibited ~91 and ~56 % improvement in flexural strength and modulus than neat novolac epoxy based Kevlar composite. Enhanced flexural properties of nanocomposites evidenced the better interface between fibers and matrix and stresses are successfully transferred through the interface. PVB dispersed in the novolac epoxy matrix very similar to the rubber particles and lowers the cross link density of novolac epoxy resin by imparting ductility to the brittle novolac epoxy resin. The rubbery particles of PVB in novolac epoxy matrix causes plastic deformation of the matrix which dissipates energy and ultimately increases the fracture energy of the composites.

#### *Impact strength*

Impact strength of all Kevlar-novolac epoxy nanocomposites are presented in Figure 3. All the nanocomposites showed better impact strength than neat novolac epoxy based Kevlar composite. Best impact strength is shown by

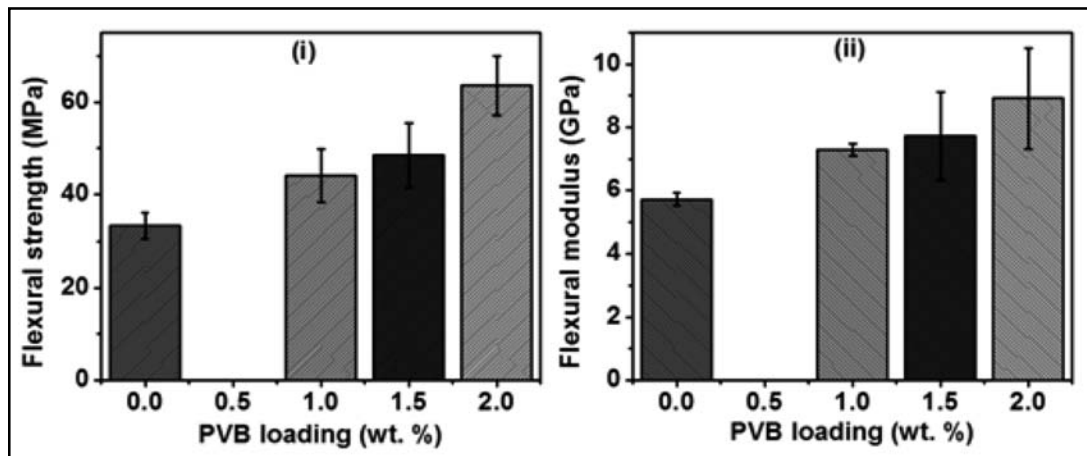


Fig. 2. (i) Flexural strength and (ii) flexural modulus of nanocomposites.

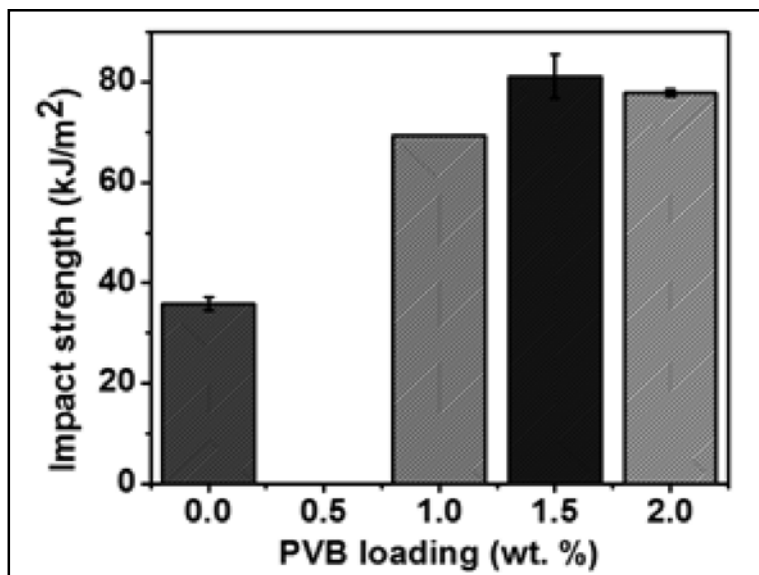


Fig. 3. Impact strength of nanocomposites.

'Composite C' (containing 0.5 wt. % f-MWCNT and 1.5 wt. % PVB). 'Composite C' exhibited ~ 126 % improvement in impact strength than that of neat novolac epoxy based Kevlar composite. Impact strength of nanocomposites increases on increasing the PVB loading up to 1.5 wt. %. Beyond 1.5 wt. % PVB (in case of 'Composite D') impact strength decreases slightly but still higher than neat novolac epoxy based Kevlar composite. Impact strength of elastomer modified novolac epoxy resin depends on the homogeneous distribution of elastomer particles in the novolac epoxy matrix. In general, elastomers have comparatively lower shear modulus than novolac epoxy matrix so stress concentration occurs at elastomer particles. When elastomers distributed homogeneously in the novolac epoxy matrix cavitation occurs and after cavitation elastomer particles dissipates energy well, consequently

the load bearing capacity of the matrix increases. In case of neat novolac epoxy based Kevlar composite delamination of sample has occurred during impact test. But in case of f-MWCNT and PVB modified novolac epoxy based Kevlar nanocomposites delamination has not been seen.

Due to the formation of cavities in the brittle novolac epoxy resin and better interfacial interaction caused by the nanoparticles, stress concentrated at the cavities and effectively transferred to the fibers. Hence, energy absorption capacity of matrix is greatly increased and it describes the improved impact strength or toughness of the Kevlar FR nanocomposites.

#### *Thermal property*

TGA and derivative thermogravimetric (DTG) curves of Kevlar FR nanocomposites are

compared in the Fig. 4 (i) and (ii). Thermal properties of all the nanocomposites are presented in Table 2. All the nanocomposites showed one step decomposition process. Onset decomposition temperature ( $T_{\text{onset}}$ ) and peak decomposition temperature ( $T_p$ ) of all the nanocomposites were improved by maximum  $\sim 40^\circ\text{C}$  and  $\sim 30^\circ\text{C}$  as compared to the neat novolac epoxy based Kevlar composite. The higher thermal stability of all the nanocomposites is attributed to the presence of small amount of f-MWCNTs which forms char during degradation process. This char restricted the evaporation of volatile decomposition products and ultimately increased the thermal stability of the nanocomposites. We have reported slight reduction in the onset decomposition temperature as the amount of PVB increased. This is due to the fact that as PVB being a

thermoplastic polymer and thermally less stable than novolac epoxy resin. Therefore, blending of PVB with novolac epoxy resin lowered the onset decomposition temperature of nanocomposites. Small weight loss in the temperature range  $30\text{--}100^\circ\text{C}$  is associated with removal of remaining solvent used for the fabrication of Kevlar based novolac epoxy composites. All the nanocomposites showed similar peak degradation temperature which is higher than neat novolac epoxy based Kevlar composite. This observation demonstrated that all the nanocomposites are thermally more stable than that of neat novolac epoxy based Kevlar composite. Higher thermal stability of nanocomposites is ascribed to the f-MWCNTs which overcome the effect of PVB on the thermal stability of nanocomposites. Residual yield of the nanocomposites was also increased as the amount of PVB increased.

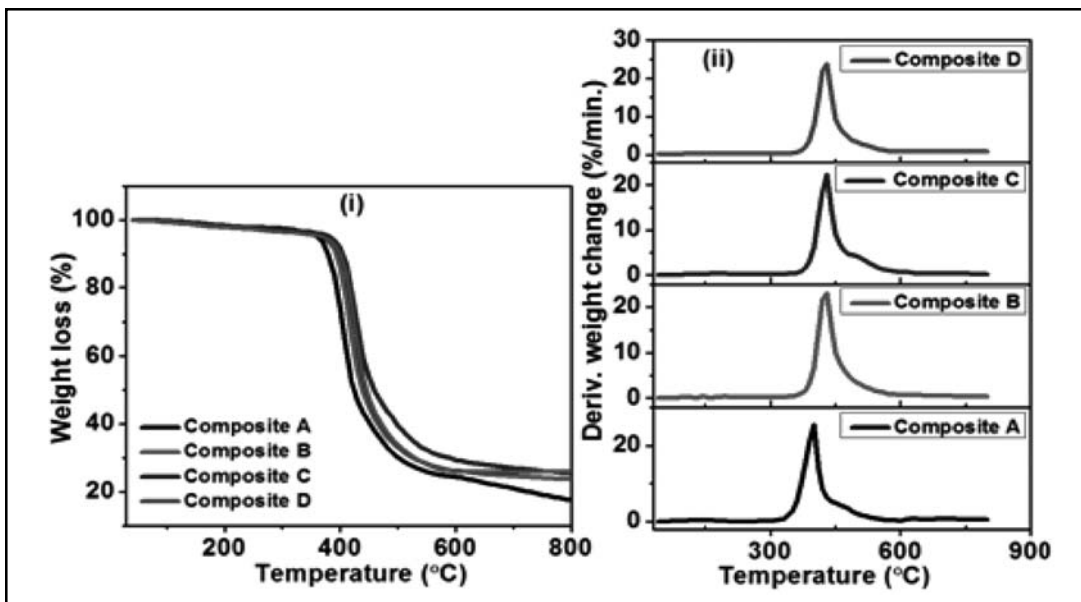


Fig. 4. (i) TGA and (ii) DTG thermograms of nanocomposites



From TGA curves of all the nanocomposites, it was observed that small weight loss (~ 5wt %) occurred in the temperature range 40-350°C due to the decomposition of the functional groups of PVB and f-MWCNTs. Main weight loss occurred between 350-450 °C in all the nanocomposites. Weight loss in this temperature range corresponded to the degradation of main chain of novolac epoxy.

TABLE 2. Thermal properties of Kevlar fiber reinforced novolac epoxy nanocomposites

Sample designation	T <sub>onset</sub> (°C)	T <sub>d</sub> (°C)	Char yield at 800°C (%)
<b>Composite A</b>	310	400	17.5
<b>Composite B</b>	355	430	23.7
<b>Composite C</b>	355	430	25.4
<b>Composite D</b>	350	430	25.9

### CONCLUSIONS

In this study, we have reported the effect of poly (vinyl butyral) on the mechanical and thermal properties of Kevlar fiber reinforced novolac epoxy/multiwalled carbon nanotube composites. Addition of small amount of poly (vinyl butyral) and f-MWCNT in the thermo setting novolac epoxy resin resulted in great improvement of flexural and impact properties of the nanocomposites. Tensile strength and modulus of nanocomposite containing 1 wt. % PVB and 0.5 wt. % multiwalled carbon nanotubes is highest among all the nanocomposites. All the nanocomposites showed superior flexural strength, flexural modulus and impact strength than neat novolac epoxy based Kevlar composite. Flexural strength and modulus of nanocomposites increases with increasing PVB loading. This was due to the flexible nature of PVB resin which on addition increases the flexibility and matrix adhesion to fibres. However, the impact strength of nanocomposites increases with increasing PVB loading up to 1.5 wt. % and

beyond this impact strength slightly decreases but still higher than neat novolac epoxy based Kevlar composite. All the nanocomposites showed higher thermal stability than neat novolac epoxy based Kevlar composite. The increment in thermal and mechanical properties is attributed to the chemical interaction between the poly (vinyl butyral) and f-MWCNT (acid group of MWCNT reacts with OH group of PVB) as reported in our recent study<sup>[27]</sup>. Therefore, they are (PVB and f-MWCNT) successfully improved the fibre–matrix interfacial interaction.

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