Light weight polymer Nano composites reinforced with h-BN for high temperature applications

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Abstract: This work presents the behavior of a polymer matrix reinforced with h-Boron Nitride (h-BN) in powder form at Nano level reinforcements, to study the strength and thermal stability aspects for high-temperature applications. Composite specimens were prepared by adding varying amount (0.1 to 0.5 wt. percentages) of reinforcements (h-BN) in the base polymer matrix (epoxy). Dispersion of h-BN was carried out using ultrasonic energy. Prepared epoxy beams were tested under tensile load and flexure to evaluate their mechanical properties such as tensile strength and load-deflection conditions. Composite material was tested using Thermo Gravimetric Analysis to study their degradation with increasing temperature. These results were compared with the plain epoxy polymer specimens. This work further investigates the ideal percentage of h-BN that gives the best results in terms of both enhanced properties and economic viability. Scanning electron microscopic testing was conducted to examine the interfacial surface adhesion between the h-BNs and the polymer matrix. Polymer composite with h-BNs 0.4% by weight showed enhanced results in strength by 49.25% when compared with plain epoxy beams due to uniform filler dispersion. It was found that addition of h-BN Nanoparticles, the material loss in the elevated temperatures has been reduced.

Keywords: h-BN Boron Nitride, Mechanical property, Thermal stability, Dispersion, TGA.

1. INTRODUCTION

Boron Nitride is a refractory compound of Boron and Nitrogen that exists in many crystalline forms. h-BN is synthesized by ambient pressure assisted chemical vapour Deposition on the poly Nitrogen. [1] It is a novel material which is highly resistant to chemical and heat. Soft matter materials are current research thrust areas for high-temperature applications [2]. Novel technology and updates in the processing of advanced polymers and their composites continue to support improvements in critical applications. Lightweight and higher performances are the prerequisites from Polymer matrix composite materials that are now inching towards moderate to high-temperature applications. Also, bio-based or natural fiber-based composites are coming into the limelight with a much thicker pace[3]. Moderate to high-temperature applications such as those of turbine engines, hot aircraft and high-speed aircraft structures. Significant attention and research have been focused on the use of epoxy polymers as thermal management solutions due to their low density, ease of manufacturing capability and a large range of applications [4].

Epoxy resins have been the pick of the substrate when it comes to mechanical, physical, chemical and many such properties [5]. Practical realization of composite materials for structural applications using Nano-scale reinforcement is gaining widespread application when compared to micro-scale fillers.
This is mainly because the Nanofillers have the unique capacity of blending of mechanical, chemical and physical properties. Polymer composites have created a lot of space in the composite world with their widespread of applications in thermal, mechanical, electrical and optical related domains, also the uniform dispersion ensures better thermal conductivity [4]. Boron Nitride is a refractory compound of Boron and Nitrogen that exists in many crystalline forms. Nano h-BN, reinforced materials are gaining more focus due to their high range of suitable properties (e.g. mechanical strength). Most recently, several researchers have produced BN Nanosheets [4], ultrathin coatings [5], nanofibers [6], Nanocrystals [7] and nanoplates [8,9]. Hexagonal boron nitride is predominantly used because of its unique mixing or blending properties in sub-constituent materials. Properties to mention few such as low density(2270kg/m$^3$), high-temperature sustainability (melting point near 2600ºC) and many more has been reported [10].

Practical realization of composite materials for structural applications using Nano-scale reinforcement is gaining widespread application when compared to micro-scale fillers. Xiangnan Wu et al reported use of h-BN as reinforcement in epoxy for electronic applications and found that the thermal conductivity is increased by 227% [11]. Furthermore, Dongju Lee, Sung found that the incorporation of BNNF into Epoxy enhances the mechanical properties i.e., tensile strength by 107% [12]. However, the problem preventing with the adaption of these developed materials is restricted because of the aging and degradation of the matrix in usage at elevated temperatures. Property improvements enabled by incorporating these materials find applications in automotive, drone, defence. Hence the present work is an attempt to enhance the thermal stability of the Polymer composites using h-BN as reinforcement.

2. MATERIAL AND METHODOLOGY

This section discusses the materials used and the procedure implemented in the development of the Nano-composites and the testing of the Nano-composites as per ASTM standards. The h-BNs used in this work were industrial-grade with 99.9% purity. Reinforcement material (h-BN) properties are given in Table 1.

| Specifications | Dimensions |
|----------------|------------|
| Diameter       | 60 (nm)    |
| Purity         | 99.9 (%)   |
| Density        | 2.29 (g/cm$^3$) |
| Molecular Weight | 24.82 (gms/mol) |
| Young’s Modulus | 3500 (GPa) |
| Melting point  | 2527 (ºC)  |

2.1 Specimen Preparations

Different predefined amounts of h-BNs were used within a polymer matrix is shown in Table 2 and were varied with 0.1%, 0.2%, 0.3%, 0.4% and 0.5% to the total weight of the matrix (epoxy). The prepared mixture was poured into 230mm x 160mm x 3 mm Steel molds. The specimens were cured in a room for 24 hrs before they were de-molded.

| Sample No. | Specimen Reference | Constituents | Percentage of h-BNs by weight |
|------------|--------------------|--------------|------------------------------|
| 1          | PE                 | Plain epoxy  | Nil                          |
| 2          | S1                 | Plain epoxy + h-BNs | 0.1                  |
2.2 Experimental setup
The mechanical properties of the Nano-composite material were evaluated by fracture mechanic test. Specimen of size 40mm x 12mm x 3mm were tested by a three-point loading test as shown in Figure 1. The technical details of the test apparatus are shown in Table 3.

![Sample placements for three-point load set-up](image)

**Figure 1.** Sample placements for three-point load set-up

| Sl. No. | Facilities for tests | Specifications | Test conducted |
|---------|----------------------|----------------|----------------|
| 1.      | Load frame testing machine | Capacity=10 kN, Least count =0.01kN, Displacement=0.01mm, FSR= ±1 count, Accuracy = ± 0.1% Operating condition= 10 to 45°C, Power supply=230V,50Hz, AC mains Strain rate = 0.05mm/min | Three-point test on beams |
| 2.      | LVDTs and Displacement indicating units | Least count= 0.01mm, Range = ± 25mm Linearity and accuracy= ± 1 digit Operating temp=10 to 50oC Range=0 to 1999 micro-strains Nominal strain= 50µm/m Input resistance >1000 Ω Output Resistance= 1000 Ω Gauge factor= 1.5 to 5 Zero-point deviation = 5% |
| 3.      | Strain measuring system | | |

Ideal percentage of h-BNs by wt. % of epoxy resin necessary to reinforce properties of plain epoxy specimens, which decides structural effectiveness in terms of higher load-bearing capacity was assessed. Tensile test was carried out on the composites to assess strength deflection criteria. The
experimental results of the composite materials were compared with neat beams. Table 4 shows the specification of the micro Universal Testing Machine used for conducting the tensile tests.

| Sl. No. | Facilities for tests | Specification | Test conducted |
|---------|----------------------|---------------|----------------|
| 1       | Micro UTM            | Max cap=10kN, Least count =0.2kgf, (1.9613N) Least Count of elongation scale =1mm Grip separation=25mm-750mm Straining Rate=100 mm/min Accuracy = +/- 0.005% | Direct tension test on flat shape specimen |

### 2.3 Three-point Bending test

This test enables the assessment of the ideal percentage of h-BNs for reinforcing in epoxy beams based on three-point loading tests. This test ensures an ideal percentage of h-BNs by wt. % of epoxy required to reinforce the plain epoxy beams, which gives the higher structural efficiency in terms of load-bearing capacity.

The specimen characteristics utilized for the flexural test as per ASTM (D2344) are shown in Table 5. Details of the test specimens used for the three-point bending test are presented in Table 6. The test results of load v/s deflection is shown in Figure 2.

From Figure 2 it follows that as the percentage of h-BNs in polymer matrix increased the brittleness of the composite increased gradually. The reason for this could be that these h-BN Nanoparticles when dispersed into the base polymer Matrix form some coarse and irregular pattern. These irregular patterns will become the source for distortion or shear yielding of the Nano Composites developed [13].

| Sl. No. | Specimen Characteristics utilized for Flexural test as per ASTM (D2344) |
|---------|-------------------------------------------------|
| 1       | Size of the Specimens: 40mm x 12mm x 3 mm       |
| 2       | Epoxy resin: L-12                                |
| 3       | Percentage of h-BNs: 0.1, 0.2, 0.3, 0.4, 0.5% by weight of epoxy resins. |

| Sl. No. | Specimen           | Ultimate load (kN) | Max. Deflection (mm) | Max. Flexural stress (N/mm²) |
|---------|--------------------|--------------------|----------------------|-----------------------------|
| 1       | PE (Plain epoxy)-PE| 2.7                | 1.4                  | 360                         |
| 2       | PE+ 0.1wt.% of h-BN-C1 | 0.3            | 1.67                 | 133.33                      |
| 3       | PE+ 0.2wt.% of h-BN-C2 | 0.2            | 1.45                 | 97.125                      |
| 4       | PE+ 0.3wt.% of h-BN-C3 | 0.15           | 1.37                 | 66.6                        |
| 5       | PE+ 0.4wt.% of h-BN-C4 | 0.125          | 1.35                 | 58.275                      |
| 6       | PE+ 0.4wt.% of h-BN-C4 | 0.1            | 0.825                | 55                          |
Figure 2. Load v/s Deflection of three-point test

2.4 Tensile test
This test assist in the evaluation of an ideal percentage of h-BNs for reinforcing epoxy beams that will end up in enhancing the ductile nature of the modified beams. The specimen characteristics utilized for the tensile test are shown in Table 7. The results of the tensile tests are presented in Table 8. The tensile test results of specimens for load v/s deflection is shown in Figure 3. As the percentage of hBN filler increased till 0.4% ultimate load increased beyond which it decreased. Uniform distribution of Hbn nanofillers as seen in Figure. 4(c) is responsible for this observed increased mechanical properties trends. Higher dosage of hBN beyond 0.4% resulted into agglomeration of the Nanoparticles due to their non-uniform dispersion. Effective dispersion of higher dosage of nanoparticles can ensure improved mechanical properties and is a continued research focus area.

Table 7. Specimen Characteristics for Tensile test as per ASTM (D3039)

| Sl. No | Composition          | Size of the Specimens     | 230mm x 25mm x 3 mm |
|-------|----------------------|---------------------------|---------------------|
| 1     | Epoxy resin          |                           | L-12                |
| 2     | Percentage of h-BN   |                           | 0.1, 0.2, 0.3, 0.4, 0.5% by weight of Epoxy resin. |

Table 8. Tensile test results

| Sl. No | Composition | Ultimate load (kN) | Ultimate Tensile strength (N/mm2) |
|--------|-------------|--------------------|-----------------------------------|
| 1      | PE          | 1.36               | 24.52                             |
| 2      | PE + 0.1 wt.% of h-BN | 1.47               | 21.7                             |
| 3      | PE + 0.2 wt.% of h-BN | 1.9                | 26.98                            |
| 4      | PE + 0.3 wt.% of h-BN | 2.2                | 30.16                            |
| 5      | PE + 0.4 wt.% of h-BN | 2.7                | 35.75                            |
| 6      | PE + 0.5 wt.% of h-BN | 1.25               | 16.16                            |
3. MICRO-CHARACTERISTIC STUDY

3.1 SEM Analysis
Figure 4 (a to d) shows the SEM images of modified epoxy composites with varied reinforcements of h-BN proportions. From Figure 4 (a), for 0.2 wt. % of h-BN reinforcement in the parent matrix it is observed that due to scarcity of Nano-particle reinforcement, a minimum distribution of filler material across the parent matrix was observed. From figure 4(b), For 0.3 wt. % of h-BN reinforcement in the parent matrix, uniform distribution of filler material was observed throughout the matrix with few irregular patterns. Figure 4(c), For 0.4 wt. % of h-BN reinforcement in the holding matrix showed good polymer chain mobility which can be observed by interconnected layers with uniform dispersion all over and this has led to good mechanical properties. From figure 4(d), for 0.5 wt.% of graphene reinforcement in the holding matrix, it is observed that increase in the reinforcement of h-BN Nano-particle has led to the agglomeration of matrix leading to the poor Mechanical Properties of the specimen. The EDAX analysis was carried out to verify the amount of species in the composite material. Figure 5 shows the EDAX graph of 0.4 wt. % in the composition. Table 9 shows the different elements present in 0.4 wt. % of hBN used.

![Figure 3. Load v/s Deflection of tensile test](image-url)

![Figure 4. (a) SEM of 0.2 wt.%](image-url)

![Figure 4.(b) SEM of 0.3 wt.%](image-url)
Figure 4.(c) SEM of 0.4 wt.%  
Figure 4.(d) SEM of 0.5 wt.%  

Figure 5. EDAX image of 0.4 wt. % of h-BN in Epoxy  

Table 9. Different elements present in 0.4 wt. % of hBN  
| Element | Weight % |
|---------|----------|
| B K     | 4.2      |
| N K     | 68.32    |
| C K     | 8.44     |
| O K     | 18.62    |

3.2 Thermo Gravimetric Analysis  
The Thermo Gravimetric Analysis (TGA) was performed in the air atmosphere to conclude the thermal stability of neat epoxy and the corresponding h-BN reinforced composites. The comparison of TGA curves of different compositions is shown in figure 6. The two characteristic degradation stages appear for both Neat epoxy and its composites. The 5% degradation temperature (T d5%) of 0.4wt. % of epoxy composite is around 365.6 °C which is greater than that of neat epoxy by around 30%. The T d 5% of Neat Epoxy is around 262 °C [14].
4. CONCLUSIONS

Research on polymer-based composites for high-temperature applications is gaining prominences which are essential to substitute critical components in hot aircraft structures, turbine engine casings, and supersonic aircraft structures. The present work is an attempt in this direction to develop Polymers reinforced with h-BN for high-temperature applications.

- From an exhaustive experimental work, polymer-based composite beams reinforced with h-BNs were investigated for improved mechanical and microstructural properties.
- As the percentage of filler material increases, the tensile strength of the material increases due to the better bonding and Uniform Dispersion of h-BN particles throughout the Epoxy Matrix as seen by SEM images. This trend was found till 0.4 wt. % composition of h-BN in the Epoxy Matrix but due to the agglomeration of h-BN particles above 0.4 wt. % of h-BN the tensile Strength of the composite materials decrease steeply. The tensile strength of the Nano Composite material of 0.4 wt. % h-BN was found to be greater than the Tensile strength of neat Epoxy by 49.25%.
- In TGA it was found that by reinforcing the h-BN particles into the Epoxy matrix, the ability of the epoxy matrix to retain its weight was increased considerably. This is because of the very high heat bearing ability of h-BN particles and also by improved interfacial interactions between the Nanoparticles and the parent matrix. The initial 5% degradation was enhanced by 30% than that of neat epoxy.
- Hence this Polymer Nano Composite material can be used for applications at a higher temperature at around 350°C. This reduces the weight of the component and increases the strength. Thus this composite will be a substitute to the presently used ceramic composites.

Further scope of work in this research area involves the development of novel hybrid Nano-composites using both micro and nano constituents that could influence in the improvement of the ductile nature. Also, work towards different dispersion techniques can increase the concentration of Nanofillers.

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