Research Article

Tensile and flexural properties of MWCNT-COOH and hBN integrated polyamide 66/short glass fiber composites

Özgür Demircan*[1, 2, a], Naser Rezaei Ansaroudi[1, b], Fatma Burcu Uzunoğlu[2, c]

[1]Department of Metallurgical and Material Engineering, Ondokuz Mayıs University, Samsun, Turkey
[2]Department of Nanoscience and Nanotechnology, Ondokuz Mayıs University, Samsun, Turkey

Article Info	Abstract
	In this study, the effect of hexagonal boron nitride (hBN) and modified (carboxylic acid functionalized) multi-walled carbon nanotubes (MWCNTs-COOH) on tensile and flexural behaviour of 30% short glass fiber reinforced Polyamide 66 (PA 66/30SGF) is investigated. Initially, MWCNTs-COOH, hBN and MWCNTs-COOH/hBN are mechanically mixed with PA 66/30SGF granules in ethanol and stirred via a magnetic stirrer for one hour. After ethanol evaporates, MWCNTs-COOH, hBN and MWCNTs-COOH/hBN integrated granules are conditioned in an oven and the obtained granules are transferred to the plastic injection moulding machine for the fabrication process of specimens. Thus five types of specimens are produced; and their mechanical behaviors are examined by Instron 5982 test machine. The test results show that elastic modulus and flexural properties of PA 66/30SGF are improved with the addition of MWCNTs-COOH, hBN and MWCNTs-COOH+hBN.

1. Introduction

Plastic materials have been widely used in medical, biomedical, military, aerospace, structural applications and so forth [1, 2]. In the last years, production of plastics globally almost reached up to 370 million tonnes [2]. However, among all plastics, thermoplastics are the most preferred given that they account for virtually 80% of the plastics used throughout the world [3]. Thermoplastics owe this popularity to their advantageous properties such as high strength, easy processibility, and reasonable production cost and lightweight. Yet, despite these advantages, some thermoplastics such as PA 66 might suffer from micro-cracking during use or production [4]. In order to prevent such mechanical problems, thermoplastics could be improved by micro-scale or nano-scale reinforcing fillers. The mixtures of polymers with inorganic or organic fillers that have certain geometries (fibers, flakes, spheres, and particulates) are known as polymer composites and if these fillers are of nano-scale dimensions, the materials are known as polymer nanocomposites [5].

In polymer matrix composites, short glass fiber (SGF) has been frequently used as reinforcing filler due to its relatively low cost and superior mechanical properties [6]. Additionally, nano-scale materials provide considerable enhancement in mechanical properties of the polymers. However, in fabrication process of polymer matrix composites or nanocomposites, achieving the uniform dispersion of the fillers in the polymer could

1

even be a lot challenging due to the fact that some nano-scale fillers tend to form bundles or agglomerates in the polymer matrix [7].

Polyamide 66 (PA 66), also known as Nylon 66, is a semi-crystalline commercial thermoplastic mostly used as engineering resin in high-performance applications where good mechanical, chemical and thermal properties are required [8, 9]. With the addition of various fillers or nano-fillers, such as glass fibers, carbon fibers, carbon nanotubes, nano clays, mechanical properties of PA 66 could be altered. Among a variety of fillers, glass fibers are extensively preferred owing to their ability of increasing the stiffness and heat resistance of the composite as well as their relatively low processing costs [10]. Addition of glass fibers into PA 66 matrix up to a certain ratio leads to a large amount of improvement in the mechanical properties [11-18].

For the last a few decades, various nanomaterials, such as single-walled or multi-walled carbon nanotubes, nanoclays, boron nitride nanoparticles and so forth, have become commercially available. A number of studies revealed that multi-walled carbon nanotubes could be ideal candidates for polymer reinforcement owing to their high tensile strength, which is 11-63 GPa [19], and Young's modulus reaching up to 1 TPa [19, 20].

Regarding CNT/polyamide composites, a number of investigations have been carried out so far [21-35] and majority of them state that CNTs are able to enhance the mechanical performance of polymeric composite systems. Miyagawa et al. [36] and Coleman et al. [37] produced overall reviews on the mechanical reinforcement of polymers by the use of CNTs. And some studies focusing on CNT-polymer matrix interaction and crack behaviour of CNTs/polymer composites are also available in literature [38-42]. Mechanical and morphological investigations demonstrated that CNTs prevent crack opening and propagation by stretching across the cracks during the fracture and hence improves the mechanical performance. Ajayan et al. [43] and Liu et al. [44] obtained the SEM images indicating the bridging phenomenon of CNTs in polymeric matrices. Zhang et al. [45] investigated the mechanical properties of MWCNT/Polyamide 6 composite prepared by simple melt-compounding and revealed that the tensile strength and the elastic modulus of the composite increase by nearly 120% and 115%, respectively, with the addition of 1 wt.% MWNTs content. This significant enhancement in mechanical performance was attributed to uniform dispersion of MWNTs in the polymer matrix and the strong interaction between MWNTs' surface and polymeric matrix. Similarly, Ferreira et al. [46] explored that the presence of 1 wt.% pristine-CNT in PA 6 matrix increases the elastic modulus by 43% and the tensile strength by 33%.

A vast majority of the studies on polymeric nanocomposites point out that mechanical behaviour of the CNT/polymer composites are highly dependent on the dispersion, distribution and alignment of CNTs throughout the matrix and the interfacial interaction between CNT and polymer [22, 32, 47-50].

Despite the high reinforcing potential of CNTs, it is extremely difficult to have them well-dispersed in the polymer due to their agglomeration tendency caused by their long length and high polarizability as well as the van der Waals forces between their surfaces [51, 52]. Agglomerated CNTs may cause stress concentrations and act like defects, which brings about reduction in mechanical performance. One of the most effective ways to avoid CNT agglomeration and achieve efficient load transfer between matrix and CNT network is functionalization [22, 30, 37, 51]. Chopra et al. [53] carried out a study on functionalized-MWCNTs/PA 6 composites and reported that the inclusion of functionalized-MWCNTs (MWCNTs-COOH) increases the tensile strength of Polyamide 6 by almost 12%. The authors explained this improvement by efficient interaction between well-dispersed MWCNTs and Polyamide 6 matrix. The study of Chen et al. [27] on the properties of PA 66/MWCNTs-COOH fibers showed that tensile strength of PA 66 fibers improves by 24%,

2

when 1 wt.% MWNTs-COOH is incorporated. This effect was attributed to the homogeneous dispersion of MWNTs in PA 66 matrix.

In recent years, thanks to the developments in nanoscience and nanotechnology, new nanomaterials have been introduced to the market and one of the most prominent of them is hexagonal boron nitride (hBN) [54], which is a 2D crystal material composed of equal boron and nitrogen atoms in a honeycomb arrangement [55-57]. Due to its structural similarity to graphene and novel properties such as excellent thermal stability, chemical inertness and high strength, hBN has become the subject of many studies to date [57-59]; and it is considered to be a potential reinforcement for polymer matrix composites. Mortazavi and Cuniberti [60] calculated the elastic modulus and tensile strength of pristine hBN films as 800-850 GPa and 150±15 GPa, respectively. Similar results regarding the mechanical properties of hBN were also presented by several authors in literature [61-64]. In addition, Joy et al. [65] provided an overall review on boron nitride based polymer nanocomposites.

Nanofillers such as nanoparticles and nanoplatelets could alter the direction of crack propagation and thereby stop the crack propagation and crack pinning along the original direction [66], which improves the mechanical performance of the composite system. According to the computational study of Spanos and Anifantis [62], even small volume fractions of boron nitride nano sheet (BNNS) can significantly contribute to the reinforcement of matrix material. The authors pointed out that sufficient interface, matrix stiffness and BNNS size and volume fraction are the critical parameters determining the elastic mechanical properties of BNNS-based nanocomposites. Similiarly, the study of Muralidhara et al. [67] revealed that presence of hBN results in increment in mechanical properties of CF filled epoxy. Moreover, Randhawa and Patel [68] reported that tensile strength and modulus of PA 6 increased by 15.2% and 64.5%, respectively, after the addition of 8 wt.% hBN.

Despite the large number of research on polymer nanocomposites in literature, to the best of our knowledge, merely a few of them discuss the mechanical performance of the composites filled with binary or ternary hybrid reinforcements. Thus, this paper aims to present the tensile and flexural properties of the nanocomposites consisting of PA 66 matrix and glass fiber+MWCNTs-COOH+hBN hybrid fillers. The results obtained in this study are expected to make a contribution to the relevant fields of science and technology in designing high-performance nanocomposites.

2. Experimental

2.1. Composite Constituents

Neat PA 66 and 30 wt.% short fiber reinforced PA 66 (PA 66/30SGF) granules used as matrix materials were purchased from Mat Polymer, Istanbul/Turkey. MWCNTs-COOH with a mass purity of more than 95%, 2.00 wt.% COOH-content, outer diameter from 10 to 20 nm, interior diameter from 5 to 10 nm, length from 10 to 30 μm, were purchased from Ege Nanotek Kimya Sanayi, Izmir/Turkey. hBN with size of 300-400 nm were supplied by the National Boron Research Institute (BOREN), Ankara/Turkey.

2.2. Fabrication Method

Specimen preparation process of hBN integrated PA 66/30SGF hybrid composites are demonstrated in Figure 1 (a) to (g). MWCNTs-COOH and/or hBN integrated composite specimens were also prepared through the same method and instruments. The list of the produced specimens and the labels assigned to them are shown in Table 1.

Table 1. List of the composite specimens

Labels	Specimens
C1	Neat PA 66
C2	PA 66/30SGF
C3	0.4 wt.% MWCNT-COOH integrated PA 66/30SGF
C4	0.4 wt.% hBN integrated PA 66/30SGF
C5	0.2 wt.% MWCNT-COOH + 0.2 wt.% hBN integrated PA 66/30SGF

Firstly, C2 granules were mixed with MWCNTs-COOH and hBN in different beakers and stirred in ethanol for one hour by means of a hot plate magnetic stirrer. After ethanol vaporized, 0.4 wt.% MWCNTs-COOH integrated C2 and 0.4 wt.% hBN integrated C2 granules were obtained. By following the same steps, 0.2 wt.% MWCNTs-COOH + 0.2 wt.% hBN integrated C2 granules were produced. These three types of granules, as well as C1 and C2 granules, were conditioned in an oven at 100 °C for 2 hours and transferred to the plastic injection moulding machine for the production of specimens. During this process, the granules fed to the funnel of the machine proceeded towards the nozzle passing through three hot zones, in which the temperature was approximately 285 °C, via a rotating screw. Owing to this high-temperature and the rotation of the screw in the hot zones, MWCNTs-COOH and hBNs efficiently mixed in C2 matrix.
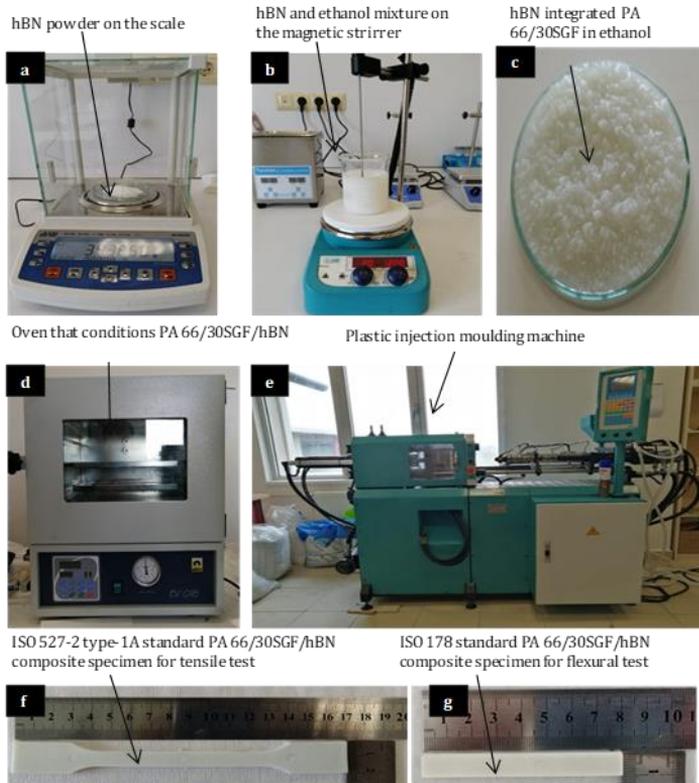

Fig. 1 Preparation process of PA 66/30SGF/hBN composite specimens

2.3. Characterization

During the plastic injection moulding process, five types of composite specimens in accordance with ISO 527-2 type-1A and ISO 178 standards were produced. Tensile and flexural properties of the specimens were analysed using Instron 5982 100 KN (USA) test machine at room temperature with a crosshead speed of 5mm/min. Scanning electron microscopy (SEM) images were obtained in a JSM-7001 F analytical field-emission SEM (Japan). Chemical structures of the specimens were analysed by Perkin Elmer Spectrum Two Fourier transform infrared spectrometer.

3. Results and Discussion

3.1. Surface Characteristics of the Fractured Composite Specimens

Figure 2 (a) to (c) represents the SEM images of the surface morphology of the fractured C3 specimen. Agglomerated MWCNT-COOH can be clearly seen in Figure 2 (b) and (c). When used as reinforcement material, CNTs stretch or bridge across the cracks and absorb the fracture energy; thus, they prevent crack opening and propagation during the fracture. This stretching behaviour of CNTs was monitored in some studies [44, 69, 70]. Moreover, in the hybrid reinforced composite systems where CNTs and fibers are used together as filler material, CNTs can create an interconnecting effect between the fiber and matrix, which leads to improvement in mechanical properties.

Figure 2 (b) demonstrates that MWCNTs-COOH are strongly embedded within C1 matrix, which is the evidence of strong interfacial adhesion between MWCNTs-COOH and the matrix. However, entangled MWCNTs-COOH or agglomerates were also observed in Figure 2 (c). They limit the mobility of PA 66 chains and hence decrease the crystallinity and confinement effect deployed by the MWCNTs-COOH [71, 72]. Despite the presence of embedded MWCNTs-COOH, agglomerated MWCNTs-COOH may cause stress concentrations and act as defects; which may lead to deterioration in mechanical properties.
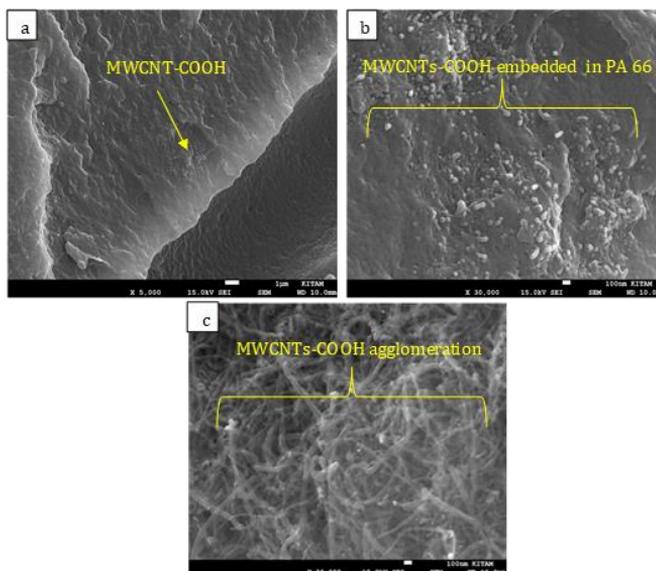

Fig. 2 SEM images of (a) fractured C3; (b) MWCNTs-COOH embedded in C1 matrix; (c) MWCNTs-COOH agglomeration

SEM images of surface morphology of fractured C4 are shown in Figure 3 (a) to (d). There is a certain amount of hBN to absorb the fracture energy and stop the crack propagation and crack pinning [60]. However, as indicated in Figure 3 (d), agglomerated hBN particles may act as defects and thereby contribute to the occurrence of microcracks within the composite system.
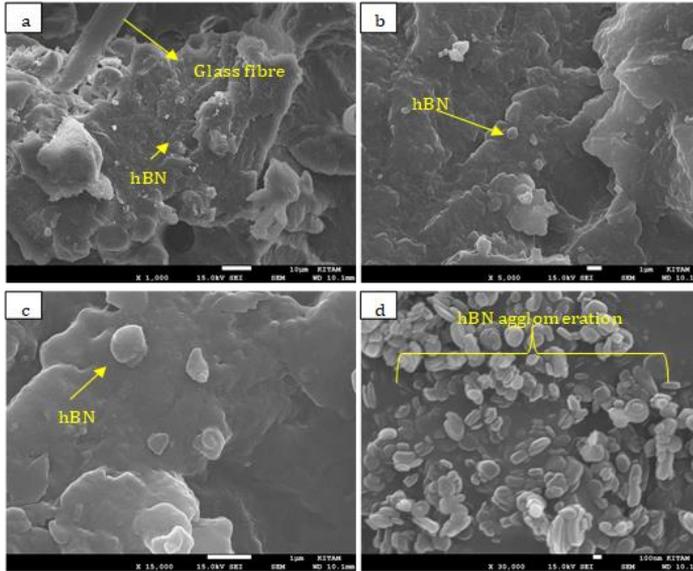

Fig. 3 SEM images of (a) fractured C4; (b) and (c) individual hBN particles; (d) hBN agglomeration

Figure 4 (a) to (c) represent the SEM images of surface morphology of fractured C5 specimen. Agglomerated hBN particles were observed, as shown in Figure 4 (a). Figure 4 (b) and Figure (c) show that MWCNTs-COOH are strongly embedded in PA 66, which indicates that an sufficient surface interaction between MWCNTs-COOH and the PA 66 matrix is achieved. However, Figure 4 (c) demonstrates a few MWCNTs-COOH pull-out probably due to the fracture or poor interfacial interaction between MWCNTs-COOH and PA 66. When the fracture ends, CNTs somewhat close and loosen getting a worm-like form, as shown by yellow arrow in Figure 4 (c). This worm-like form is due to the relaxation or uneven crack propagation [40]. On the other hand, no direct interaction between MWCNT-COOH and hBN was observed.
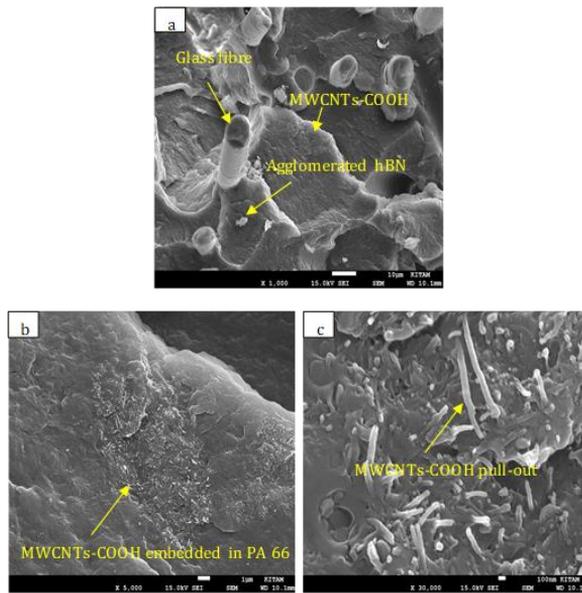
Fig. 4 SEM images of (a) fractured C5; (b) MWCNTs-COOH embedded in PA 66; (c) MWCNTs-COOH pull-out

3.2. Chemical Analysis

Understanding the chemical structure of the components in a material is quite useful so as to achieve good mechanical properties by controlling the process parameters. From Fourier Transform Infrared (FTIR) spectra of the injection-moulded composite specimens, shown in Figure 5, it can be seen that the signature regions do not exhibit a significant difference by the addition of micro- and nano-scale fillers. In neat PA 66, the absorption band at 3267 cm^{-1} is correlated to the stretching vibrations of N-H group. The absorption bands at 2912 cm^{-1}, 2843 cm^{-1} and 1192 cm^{-1} stem from the symmetric and asymmetric C–H stretching vibrations and C–H twisting. The peaks appearing at 1636 cm^{-1} and 1545 cm^{-1} are assigned to the stretching vibration of the C=O group of the amide I and the N–H bending and C–N stretching vibration of amide II, respectively. The peak at 1283 cm^{-1} is associated with C–N–H coupling vibration of amide III. The presence of glass fibers does not bring about a significant change in the molecular structure of PA 66, which could be due to the lack of chemical interaction between glass fibers and PA 66 matrix [63].
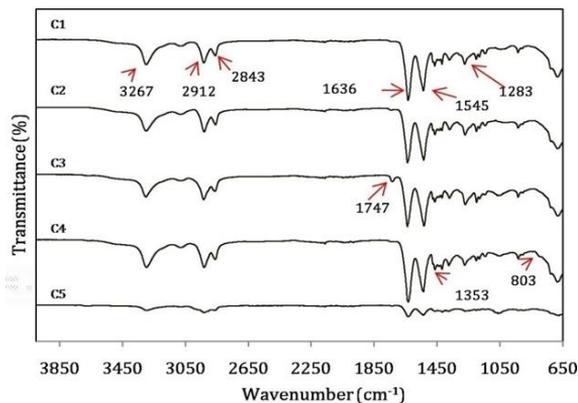
Fig. 5 FTIR spectra of the specimens

In Figure 5 (c), the absorption band at 1747 cm−1 results from C=O symmetric stretching of carboxyl, which confirms the presence of MWCNT-COOH. Similar observations were also made by Al-Hobaib et al. [64] and Chen et al. [26]. And also, considering the observations made by B. Zhang et al. [65], characteristic peaks of hBN at 1353 cm−1 and 803 cm−1 shown in Figure 5 (d) can be correlated to in-plane B-N stretching and out-of-plane B-N bending vibrations of hBN, respectively. The appearance of the characteristic peaks of carboxyl group of MWCNT-COOH and hBN indicates that no chemical reaction occurred during the melting and mixing step of plastic injection process. Therefore, physical interactions alone are likely to be responsible for any change in the mechanical properties of the composite system. Yet, considering the study by Demircan et al. [66], due to the high-temperature (nearly 285°C) in the hot zones of the plastic injection machine chemical interaction at some level might have occurred.

3.3 Tensile Test Results

Load-displacement curves and the tensile-fractured specimens are represented in Figure 6 (a) and (b) respectively. As shown in Figure 6 (c), C2 exhibits the highest tensile strength (87.05 MPa) whereas C5 exhibits the highest elastic modulus (5.17 GPa). The graphs demonstrate that the inclusion of glass fibers improves the tensile strength and elastic modulus of C1. This result is in accordance with the results of relevant studies in literature [10-12, 15, 17]. However, the addition of 0.4 wt.% MWCNTs-COOH into C2 leads to reduction by 28% in tensile strength while increasing the elastic modulus by 14.7%. This failure can be explained by the agglomeration of MWCNTs-COOH in the matrix. Similarly, presence of 0.4 wt.% hBN in C2 increases the elastic modulus by nearly 11.2% and reduces the tensile strength by 20.6%. The findings of some relevant studies in literature support these results [69, 77-80].

Considering the number of similar investigations in literature, it can be claimed that mechanical performance of hybrid composites incorporating ternary fillers has not been fully revealed yet. However, the present study revealed that the addition of MWCNTs-COOH and hBN together increases the elastic modulus of C2 by 15.4% and decreases the tensile strength of it by 13.33%. It is obvious that C3 exhibits better tensile performance over C4. Moreover, the addition of MWCNTs-COOH and hBN together further improves the tensile properties, which indicates that these two nanomaterials are compatible with each other in a ternary-filler polymeric composite system.
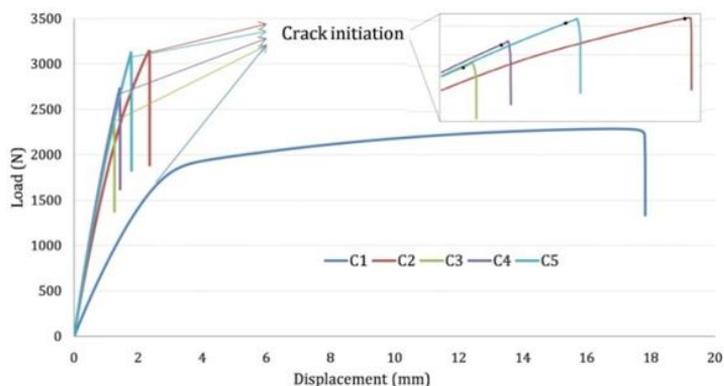
(a)

(b)
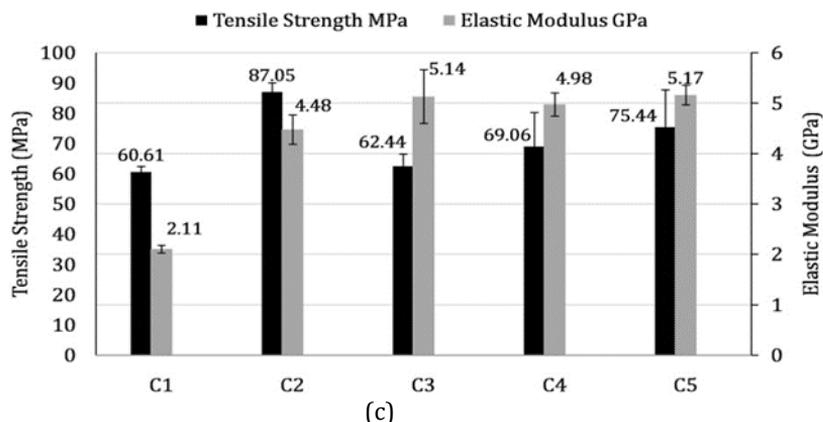
(c)

Fig. 6 (a) Load-displacement curves of the specimens after tensile tests; (b) Tensile-fractured specimens; (c) Tensile properties of the specimens

3.4 Flexural Test Results

Figure 7 (a) and (b) represent the load-displacement curves after 3-point flexural tests and the fractured specimens, respectively. According to the results, shown in Figure (c), C5 exhibits the highest flexural strength (170.48 MPa) and flexural modulus (3.89 GPa) whereas C1 exhibits the lowest flexural strength (65.33 MPa) and flexural modulus (1.07 GPa). It is clear that the presence of short glass fibers enhances the flexural performance of C1. As aforementioned, this improvement can be attributed to the good mechanical properties of glass fibers as well as their homogeneous distribution in the matrix. With the addition of 0.4 wt.% MWCNTs-COOH, flexural strength and flexural modulus of C2 increase by nearly 7% and 13%, respectively. This positive effect can be explained by the fact that

CNTs prevent crack opening and propagation by bridging across the cracks during the fracture. Moreover, they cause an interlocking effect between fibers and matrix and thereby improve the flexural and tensile properties of the composite system.
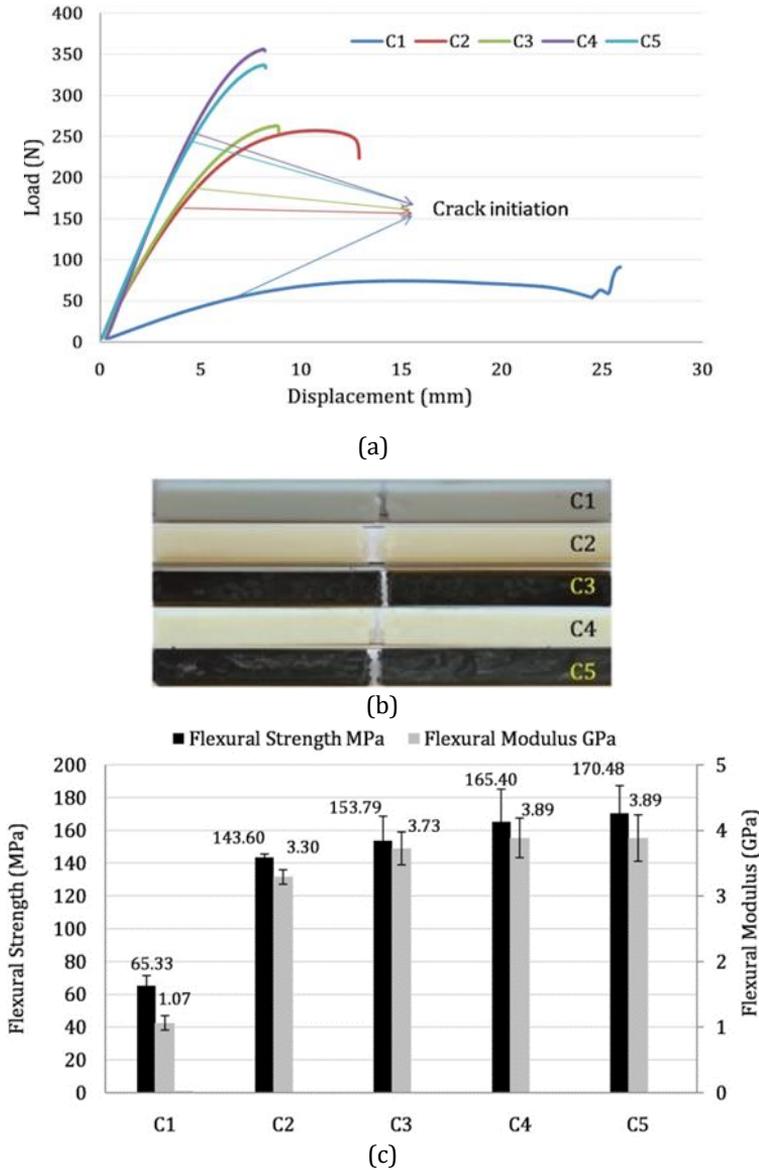

(a)

(b)

(c)

Fig. 7 (a) Load-displacement curves of the specimens after three-point flexural tests; (b) Flexural-fractured specimens; (c) Flexural properties of the specimens

In the present study, 0.4 wt.% hBN integration results in better flexural performance over that with 0.4 wt.% MWCNTs-COOH whereas the composite with 0.2 wt.% MWCNTs-COOH + 0.2 wt.% hBN fillers exhibits the best flexural performance. Since good filler-matrix facial interaction allows the fillers to absorb the fracture energy and thus contributes to the enhancement in mechanical properties, the improvement in flexural properties can be attributed to the good surface interaction between the fillers and the PA

66 matrix. Similar results were obtained and discussed in a number of studies in literature [80, 88].

Figure 8 (a) to (d) represents the optical micrographs of fractured specimens after 3-point flexural tests. Failure modes of the specimens were mainly matrix cracks along the direction of tension. Longer cracks were observed in fractured C2.
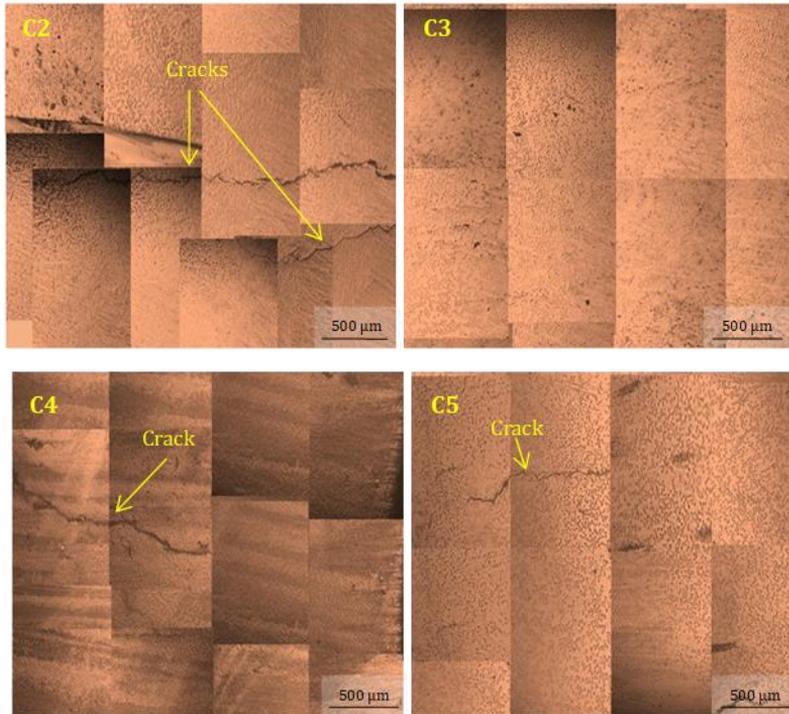

Fig. 8 Optical micrographs of fractured C2, C3, C4 and C5

5. Conclusions

In this study, mechanical properties of MWCNT-COOH and/or hBN integrated PA 66/30SGF composites were investigated. Mechanical analyses showed that the presence of short glass fibers positively influences the tensile and flexural performance of PA 66. This behavior can be explained by good mechanical properties of glass fibers and their sufficient facial interaction with the matrix surface.

The obtained test results demonstrated that the highest tensile strength and elastic modulus were exhibited by PA 66/30SGF and MWCNTs-COOH+hBN integrated PA 66/30SGF composite specimens, respectively. However, it was observed that the addition of MWCNTs-COOH and hBN leads to deterioration in the tensile strength. Since the desired reinforcement highly depends on the uniform stress transfer between the filler and matrix, we can conclude that the external stress applied to the specimens incorporating MWCNTs-COOH was not well distributed along the matrix due to the presence of agglomerates; consequently, the tensile strength decreased.

On the other hand, addition of MWCNTs-COOH and hBN enhanced the flexural properties of PA 66/30SGF composites. Having tubular form, MWCNTs are able to stretch across the cracks absorbing the fracture energy and hence prevent crack opening and propagation.

Besides this bridging phenomenon, MWCNTs can cause interlocking effect between the fiber and matrix and prevent glass fibers from slipping, which improve the mechanical performance of the composite system. hBN particles, on the other hand, can stop crack propagation and crack pinning by changing the direction of crack propagation and hence make a contribution to the mechanical properties. The specimens with 0.4 wt.% hBN exhibit higher mechanical performance than that with 0.4 wt.% MWCNTs-COOH, which might be due to their mechanical and geometrical or morphological differences as well as the difference in their agglomeration tendency. The highest flexural values were found in specimens where MWCNTs-COOH and hBN were integrated together; therefore, we can conclude that the hybrid reinforcement mechanism worked efficiently and that MWCNT-COOH and hBN are compatible with each other. The shorter cracks in MWCNT-COOH and hBN filled PA 66/SGF observed by optical microscopy confirm this conclusion.

FTIR spectra of the specimens confirmed the molecular structure of PA 66 as well as the presence of MWCNT-COOH and hBN in the system. It was also observed that glass fibers do not bring about a drastic change in the chemical structure of PA 66. Although a chemical interaction due to the high temperature applied in the specimen production process might have occurred, since no significant chemical bond was detected, the increase in mechanical properties are dominantly due to the physical interactions.

Considering the increments in elastic modulus, flexural modulus and flexural strength of the specimens, MWCNT and hBN integrated PA 66/glass fiber composites are expected to be quite promising for future applications in which high mechanical performance is required.

Acknowledgement

References

[1] Ching YC, Chuah CH, Ching KY, Abdullah LC, Rahman A. Applications of thermoplastic-based blends. Recent Developments in Polymer Macro, Micro and Nano Blends2017. p. 111-29. https://doi.org/10.1016/B978-0-08-100408-1.00005-4
[2] Europe P. Plastics-the Facts 2020 An analysis of European plastics production, demand and waste data Brussels: Plastics Europe; 2020 [Available from: https://www.plasticseurope.org.
[3] Dynisco. Understanding Plastics and Polymers - The Different Types of Plastic: AZoM; 2019 [Available from: https://www.azom.com/article.aspx?ArticleID=17477 .]
[4] Awaja F, Zhang S, Tripathi M, Nikiforov A, Pugno N. Cracks, microcracks and fracture in polymer structures: Formation, detection, autonomic repair. Progress in Materials Science. 2016;83:536-73. https://doi.org/10.1016/j.pmatsci.2016.07.007
[5] Xanthos M. Polymers and Polymer Composites. Functional Fillers for Plastics. Second ed. 2010. p. 1-18. https://doi.org/10.1002/9783527629848.ch1
[6] Hamerton I. Book Review: Functional Fillers for Plastics. By Marino Xanthos (Ed.). Advanced Materials, 2006;18:248-. https://doi.org/10.1002/adma.200500797
[7] Rangari V. Polymer Nanocomposite Materials for Structural Applications. Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications2011. https://doi.org/10.5772/15615
[8] Chow WS, Mohd Ishak ZA. Polyamide blend-based nanocomposites: A review. Express Polymer Letters. 2015;9(3):211-32. https://doi.org/10.3144/expresspolymlett.2015.22

[9] Gilbert M. Chapter 18 - Aliphatic Polyamides. In: Gilbert M, editor. Brydson's Plastics Materials (Eighth Edition): Butterworth-Heinemann; 2017. p. 487-511. https://doi.org/10.1016/B978-0-323-35824-8.00018-9

[10] Zhou Y, Mallick PK. A non-linear damage model for the tensile behavior of an injection molded short E-glass fiber reinforced polyamide-6,6. Materials Science and Engineering: A. 2005;393(1):303-9. https://doi.org/10.1016/j.msea.2004.10.038

[11] Javangula S, Ghorashi B, Draucker CC. Mixing of glass fibers with nylon 6,6. Journal of Materials Science. 1999;34(20):5143-51. https://doi.org/10.1023/A:1004777520458

[12] Srivastava VK, Lal S. Mechanical properties of E-glass fiber reinforced nylon 6/6 resin composites. Journal of Materials Science. 1991;26(24):6693-8. https://doi.org/10.1007/BF0240266

[13] Kagan V, McPherson R, Chung J. An Advanced High Modulus (HMG) Short Glass-Fiber Reinforced Nylon 6: Part I - Role and Kinetic of FiberGlass Reinforcements. Journal of Reinforced Plastics and Composites. 2003; 22:1035-44. https://doi.org/10.1177/0731684403023285

[14] Çuvalci H, Erbay K, İpek H. Investigation of the Effect of Glass Fiber Content on the Mechanical Properties of Cast Polyamide. Arabian Journal for Science and Engineering. 2014;39(12):9049-56. https://doi.org/10.1007/s13369-014-1409-8

[15] Lingesh BV, Rudresh BM, Ravikumar BN. Effect of Short Glass Fibers on Mechanical Properties of Polyamide66 and Polypropylene (PA66/PP) Thermoplastic Blend Composites. Procedia Materials Science. 2014;5:1231-40. https://doi.org/10.1016/j.mspro.2014.07.434

[16] Kim J-W, Kim H-S, Lee D-G. Tensile Strength of Glass Fiber-Reinforced Plastic by Fiber Orientation and Fiber Content Variations. International Journal of Modern Physics: Conference Series. 2012;06:640-5. https://doi.org/10.1142/S201019451200390X

[17] Autay R, Mars J, Fakhreddine D. Mechanical and tribological study of short glass fiber-reinforced PA 66. Polymers and Polymer Composites. 2019;27. https://doi.org/10.1177/0967391119853956

[18] Nuruzzaman DM, Iqbal AKMA, Oumer AN, Ismail NM, Basri S. Experimental investigation on the mechanical properties of glass fiber reinforced nylon. IOP Conference Series: Materials Science and Engineering. 2016;114. https://doi.org/10.1088/1757-899X/114/1/012118

[19] Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. Science. 2000;287(5453):637-40. https://doi.org/10.1126/science.287.5453.637

[20] Salvetat J-P, Briggs G, Bonard J-M, Bacsa R, Kulik A, Stöckli T, et al. Elastic and Shear Moduli of Single-Walled Carbon Nanotube Ropes. Physical Review Letters. 1999;82(5):944-7. https://doi.org/10.1103/PhysRevLett.82.944

[21] Arash B, Wang Q, Varadan VK. Mechanical properties of carbon nanotube/polymer composites. Sci Rep. 2014;4:6479. https://doi.org/10.1038/srep06479

[22] Sahoo NG, Rana S, Cho JW, Li L, Chan SH. Polymer nanocomposites based on functionalized carbon nanotubes. Progress in Polymer Science. 2010;35(7):837-67. https://doi.org/10.1016/j.progpolymsci.2010.03.002

[23] Tarfaoui M, Lafdi K, El Moumen A. Mechanical properties of carbon nanotubes based polymer composites. Composites Part B: Engineering. 2016;103:113-21. https://doi.org/10.1016/j.compositesb.2016.08.016

[24] Moniruzzaman M, Chattopadhyay J, Billups WE, Winey KI. Tuning the mechanical properties of SWNT/nylon 6,10 composites with flexible spacers at the interface. Nano Lett. 2007;7(5):1178-85. https://doi.org/10.1021/nl062868e

[25] Coleman JN, Khan U, Blau WJ, Gun'ko YK. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. Carbon. 2006;44(9):1624-52. https://doi.org/10.1016/j.carbon.2006.02.038

[26] Jin F-L, Park S-J. A review of the preparation and properties of carbon nanotubes-reinforced polymer compositess. Carbon letters. 2011;12(2):57-69. https://doi.org/10.5714/CL.2011.12.2.057

[27] Chen T, Liu H, Wang X, Zhang H, Zhang X. Properties and Fabrication of PA66/Surface-Modified Multi-Walled Nanotubes Composite Fibers by Ball Milling and Melt-Spinning. Polymers (Basel). 2018;10(5). https://doi.org/10.3390/polym10050547

[28] Hassani AJ, Mohd Ishak ZA, Mohamed AR. Preparation and characterization of polyamide 6 nanocomposites using MWCNTs based on bimetallic Co-Mo/MgO catalyst. Express Polymer Letters. 2014;8(3):177-86. https://doi.org/10.3144/expresspolymlett.2014.21

[29] Zhang J, Gao X, Zhang X, Liu H, Zhang H, Zhang X. Polyamide 66 and amino-functionalized multi-walled carbon nanotube composites and their melt-spun fibers. Journal of Materials Science. 2019;54(16):11056-68. https://doi.org/10.1007/s10853-019-03619-0

[30] Spitalsky Z, Tasis D, Papagelis K, Galiotis C. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. Progress in Polymer Science. 2010;35(3):357-401. https://doi.org/10.1016/j.progpolymsci.2009.09.003

[31] Khan W, Sharma R, Saini P. Carbon Nanotube-Based Polymer Composites: Synthesis, Properties and Applications. Carbon Nanotubes - Current Progress of their Polymer Composites2016. https://doi.org/10.5772/62497

[32] Zabegaeva ON, Sapozhnikov DA, Buzin MI, Krestinin AV, Kotelnikov VA, Baiminov BA, et al. Nylon-6 and single-walled carbon nanotubes polyamide composites. High Performance Polymers. 2016;29(4):411-21. https://doi.org/10.1177/0954008316645848

[33] Song Y, Zheng N, Dong X, Gao J. Flexible Carboxylated CNT/PA66 Nanofibrous Mat Interleaved Carbon Fiber/Epoxy Laminates with Improved Interlaminar Fracture Toughness and Flexural Properties. Industrial & Engineering Chemistry Research. 2020;59(3):1151-8. https://doi.org/10.1021/acs.iecr.9b05854

[34] Kumar A, Sharma K, Dixit AR. A review on the mechanical properties of polymer composites reinforced by carbon nanotubes and graphene. Carbon Letters. 2021;31(2):149-65. https://doi.org/10.1007/s42823-020-00161-x

[35] Kang S, Kim J, Park JH, Jung I, Park M. Multiwalled carbon nanotube pretreatment to enhance tensile properties, process stability, and filler dispersion of polyamide 66 nanocomposites. Composites Part B: Engineering. 2020;198:108204. https://doi.org/10.1016/j.compositesb.2020.108204

[36] Miyagawa H, Misra M, Mohanty AK. Mechanical properties of carbon nanotubes and their polymer nanocomposites. J Nanosci Nanotechnol. 2005;5(10):1593-615. https://doi.org/10.1166/jnn.2005.181

[37] Coleman JN, Khan U, Gun'ko YK. Mechanical Reinforcement of Polymers Using Carbon Nanotubes. Advanced Materials. 2006;18(6):689-706. https://doi.org/10.1002/adma.200501851

[38] Gorga RE, Lau KKS, Gleason KK, Cohen RE. The importance of interfacial design at the carbon nanotube/polymer composite interface. Journal of Applied Polymer Science. 2006;102(2):1413-8. https://doi.org/10.1002/app.24272

[39] Gupta AK, Harsha SP. Effect of crack and determination of fracture energy of carbon nanotube-reinforced polymer composites. Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems. 2014;229(3):110-6. https://doi.org/10.1177/1740349914531758

[40] Shindo Y, Kuronuma Y, Takeda T, Narita F, Fu S-Y. Electrical resistance change and crack behavior in carbon nanotube/polymer composites under tensile loading. Composites Part B: Engineering. 2012;43(1):39-43. https://doi.org/10.1016/j.compositesb.2011.04.028

[41] Kuronuma Y, Shindo Y, Takeda T, Narita F. Crack growth characteristics of carbon nanotube-based polymer composites subjected to cyclic loading. Engineering Fracture Mechanics. 2011;78(17):3102-10. https://doi.org/10.1016/j.engfracmech.2011.09.006

[42] Kuronuma Y, Shindo Y, Takeda T, Narita F. Fracture behaviour of cracked carbon nanotube-based polymer composites: Experiments and finite element simulations. Fatigue & Fracture of Engineering Materials & Structures. 2010;33(2):87-93. https://doi.org/10.1111/j.1460-2695.2009.01419.x

[43] Ajayan PM, Schadler L, Giannaris C, Rubio A. Single-walled carbon nanotube-polymer COMPOSITES: Strength and weakness. Advanced Materials. 2000;12:750-+. https://doi.org/10.1002/(SICI)1521-4095(200005)12:10<750::AID-ADMA750>3.0.CO;2-6

[44] Liu T, Phang IY, Shen L, Chow SY, Zhang W-D. Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. Macromolecules. 2004;37(19):7214-22. https://doi.org/10.1021/ma049132t

[45] Zhang W, Shen L, Phang I, Liu T. Carbon Nanotubes Reinforced Nylon6 Composite Prepared by Simple Melt-Compounding. Macromolecules. 2004;37:256-9. https://doi.org/10.1021/ma035594f

[46] Ferreira T, Paiva MC, Pontes AJ. Dispersion of carbon nanotubes in polyamide 6 for microinjection moulding. Journal of Polymer Research. 2013;20(11). https://doi.org/10.1007/s10965-013-0301-7

[47] Jogi BF, Sawant M, Kulkarni M, Brahmankar PK. Dispersion and Performance Properties of Carbon Nanotubes (CNTs) Based Polymer Composites: A Review. Journal of Encapsulation and Adsorption Sciences. 2012;02(04):69-78. https://doi.org/10.4236/jeas.2012.24010

[48] Pötschke P, Bhattacharyya AR, Janke A, Pegel S, Leonhardt A, Täschner C, et al. Melt Mixing as Method to Disperse Carbon Nanotubes into Thermoplastic Polymers. Fullerenes, Nanotubes and Carbon Nanostructures. 2005;13(sup1):211-24. https://doi.org/10.1081/FST-200039267

[49] Kim SW, Kim T, Kim YS, Choi HS, Lim HJ, Yang SJ, et al. Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. Carbon. 2012;50(1):3-33. https://doi.org/10.1016/j.carbon.2011.08.011

[50] Wise KE, Park C, Siochi EJ, Harrison JS. Stable dispersion of single wall carbon nanotubes in polyimide: the role of noncovalent interactions. Chemical Physics Letters. 2004;391(4-6):207-11. https://doi.org/10.1016/j.cplett.2004.04.096

[51] Ma P-C, Siddiqui NA, Marom G, Kim J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. Composites Part A: Applied Science and Manufacturing. 2010;41(10):1345-67. https://doi.org/10.1016/j.compositesa.2010.07.003

[52] Banerjee J, Dutta K. Melt-mixed carbon nanotubes/polymer nanocomposites. Polymer Composites. 2019;40(12):4473-88. https://doi.org/10.1002/pc.25334

[53] Chopra S, Deshmukh KA, Deshmukh AD, Peshwe DR. Functionalization and Melt-compounding of MWCNTs in PA-6 for Tribological Applications. IOP Conference Series: Materials Science and Engineering. 2018;346. https://doi.org/10.1088/1757-899X/346/1/012005

[54] Raman C, Meneghetti P. Boron nitride finds new applications in thermoplastic compounds. Plastics, Additives and Compounding. 2008;10:26-31. https://doi.org/10.1016/S1464-391X(08)70092-8

[55] Zhang Z, Liu Y, Yang Y, Yakobson BI. Growth Mechanism and Morphology of Hexagonal Boron Nitride. Nano Lett. 2016;16(2):1398-403. https://doi.org/10.1021/acs.nanolett.5b04874

[56] Nag A, Raidongia K, Hembram KPSS, Datta R, Waghmare UV, Rao CNR. Graphene Analogues of BN: Novel Synthesis and Properties. ACS Nano. 2010;4(3):1539-44. https://doi.org/10.1021/nn9018762

[57] Golberg D, Bando Y, Terao T, Mitome M, Tang C, Zhi C. Boron Nitride Nanotubes and Nanosheets. ACS nano. 2010;4:2979-93. https://doi.org/10.1021/nn1006495

[58] Peng Q, Ji W, De S. Mechanical properties of the hexagonal boron nitride monolayer: Ab initio study. Computational Materials Science. 2012;56:11-7. https://doi.org/10.1016/j.commatsci.2011.12.029

[59] Rasul MG, Kiziltas A, Arfaei B, Shahbazian-Yassar R. 2D boron nitride nanosheets for polymer composite materials. npj 2D Materials and Applications. 2021;5(1):56. https://doi.org/10.1038/s41699-021-00231-2

[60] Mortazavi B, Cuniberti G. Mechanical properties of polycrystalline boron-nitride nanosheets. RSC Adv. 2014;4(37):19137-43. https://doi.org/10.1039/C4RA01103A

[61] Li N, Ding N, Qu S, Liu L, Guo W, Wu C-ML. Mechanical properties and failure behavior of hexagonal boron nitride sheets with nano-cracks. Computational Materials Science. 2017;140:356-66. https://doi.org/10.1016/j.commatsci.2017.09.011

[62] Spanos KN, Anifantis NK. Mechanical characterization of hexagonal boron nitride nanocomposites: A multiscale finite element prediction. Journal of Composite Materials. 2017;52(16):2229-41. https://doi.org/10.1177/0021998317740942

[63] Qi-lin X, Zhen-huan L, Xiao-geng T. The defect-induced fracture behaviors of hexagonal boron-nitride monolayer nanosheets under uniaxial tension. Journal of Physics D: Applied Physics. 2015;48(37). https://doi.org/10.1088/0022-3727/48/37/375502

[64] Zhao S, Xue J. Mechanical properties of hybrid graphene and hexagonal boron nitride sheets as revealed by molecular dynamic simulations. Journal of Physics D: Applied Physics. 2013;46(13). https://doi.org/10.1088/0022-3727/46/13/135303

[65] Joy J, George E, Haritha P, Thomas S, Anas S. An overview of boron nitride based polymer nanocomposites. Journal of Polymer Science. 2020;58(22):3115-41. https://doi.org/10.1002/pol.20200507

[66] Sun L, Gibson RF, Gordaninejad F, Suhr J. Energy absorption capability of nanocomposites: A review. Composites Science and Technology. 2009;69(14):2392-409. https://doi.org/10.1016/j.compscitech.2009.06.020

[67] Muralidhara B, Babu SPK, Suresha B. Studies on mechanical, thermal and tribological properties of carbon fiber-reinforced boron nitride-filled epoxy composites. High Performance Polymers. 2020;32(9):1061-81. https://doi.org/10.1177/0954008320929396

[68] Randhawa KS, Patel AD. Enhancing tribo-mechanical properties and thermal stability of nylon 6 by hexagonal boron nitride fillers. e-Polymers. 2020;20(1):733-45. https://doi.org/10.1515/epoly-2020-0069

[69] Puch F, Hopmann C. Morphology and tensile properties of unreinforced and short carbon fiber reinforced Nylon 6/multiwalled carbon nanotube-composites. Polymer. 2014;55(13):3015-25. https://doi.org/10.1016/j.polymer.2014.04.052

[70] Qian D, Dickey EC, Andrews R, Rantell T. Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. Applied Physics Letters. 2000;76(20):2868-70. https://doi.org/10.1063/1.126500

[71] Chen J-y, Mao X-p, Wang G-w. Mechanical Properties of MWCNTs/PA66 Composites under Impact Loading. DEStech Transactions on Engineering and Technology Research. 2017. https://doi.org/10.12783/dtetr/ameme2016/577

[72] Reza Sanei SH, Drozynski H, Hetrick D, editors. Effect of Strain Rate on Tensile Properties of Injection Molded Multiwall Carbon Nanotube Reinforced PA 6/6 Nanocomposites. ASME 2020 International Mechanical Engineering Congress and Exposition; 2020. V003T03A015. https://doi.org/10.1115/IMECE2020-23049

[73] Lakkur Munirajappa M, Harijan Basavaraju R. Microstructural characterization of short glass fiber and PAN based carbon fiber reinforced nylon 6 polymer composites.

Polymer Engineering & Science. 2018;58(8):1428-37. https://doi.org/10.1002/pen.24737

[74]Al-Hobaib AS, Al-Sheetan KM, Shaik MR, Al-Suhybani MS. Modification of thin-film polyamide membrane with multi-walled carbon nanotubes by interfacial polymerization. Applied Water Science. 2017;7(8):4341-50. https://doi.org/10.1007/s13201-017-0578-5

[75]Zhang B, Wu Q, Yu H, Bulin C, Sun H, Li R, et al. High-Efficient Liquid Exfoliation of Boron Nitride Nanosheets Using Aqueous Solution of Alkanolamine. Nanoscale Research Letters. 2017;12(1):596. https://doi.org/10.1186/s11671-017-2366-4

[76]Demircan O, Al-darkazali A, Inanc I, Eskizeybek V. Investigation of the effect of CNTs on the mechanical properties of LPET/glass fiber thermoplastic composites. Journal of Thermoplastic Composite Materials. 2019;33:089270571983310. https://doi.org/10.1177/0892705719833105

[77]Mahmood N, Islam M, Hameed A, Saeed S, Khan AN. Polyamide-6-based composites reinforced with pristine or functionalized multi-walled carbon nanotubes produced using melt extrusion technique. Journal of Composite Materials. 2013;48(10):1197-207. https://doi.org/10.1177/0021998313484779

[78]Meng H, Sui GX, Fang PF, Yang R. Effects of acid- and diamine-modified MWNTs on the mechanical properties and crystallization behavior of polyamide 6. Polymer. 2008;49(2):610-20. https://doi.org/10.1016/j.polymer.2007.12.001

[79]Chan KW, Wong HM, Yeung KWK, Tjong SC. Polypropylene Biocomposites with Boron Nitride and Nanohydroxyapatite Reinforcements. Materials (Basel). 2015;8(3):992-1008. https://doi.org/10.3390/ma8030992

[80]Ayrilmis N, Dundar T, Kaymakci A, Ozdemir F, Kwon JH. Mechanical and thermal properties of wood-plastic composites reinforced with hexagonal boron nitride. Polymer Composites. 2014;35(1):194-200. https://doi.org/10.1002/pc.22650

[81]Goriparthi BK, Naveen PNE, Ravi Sankar H, Ghosh S. Effect of functionalization and concentration of carbon nanotubes on mechanical, wear and fatigue behaviours of polyoxymethylene/carbon nanotube nanocomposites. Bulletin of Materials Science. 2019;42(3). https://doi.org/10.1007/s12034-019-1746-z

[82]Nguyen-Tran HD, Hoang VT, Do VT, Chun DM, Yum YJ. Effect of Multiwalled Carbon Nanotubes on the Mechanical Properties of Carbon Fiber-Reinforced Polyamide-6/Polypropylene Composites for Lightweight Automotive Parts. Materials (Basel). 2018;11(3). https://doi.org/10.3390/ma11030429

[83]Mathur RB, Pande S, Singh BP, Dhami TL. Electrical and mechanical properties of multi-walled carbon nanotubes reinforced PMMA and PS composites. Polymer Composites. 2008;29(7):717-27. https://doi.org/10.1002/pc.20449

[84]Panchagnula KK, Kuppan P. Improvement in the mechanical properties of neat GFRPs with multi-walled CNTs. Journal of Materials Research and Technology. 2019;8(1):366-76. https://doi.org/10.1016/j.jmrt.2018.02.009

[85]Prolongo SG, Gude MR, Ureña A. Improving the flexural and thermomechanical properties of amino-functionalized carbon nanotube/epoxy composites by using a pre-curing treatment. Composites Science and Technology. 2011;71(5):765-71. https://doi.org/10.1016/j.compscitech.2011.01.028

[86]Salmoria GV, Paggi RA, Lago A, Beal VE. Microstructural and mechanical characterization of PA12/MWCNTs nanocomposite manufactured by selective laser sintering. Polymer Testing. 2011;30(6):611-5. https://doi.org/10.1016/j.polymertesting.2011.04.007

[87]Koilraj TT, Kalaichelvan K. Experimental Study on Mechanical Properties of PA66 Blended with MWNTs. Applied Mechanics and Materials. 2015;766-767:383-8. https://doi.org/10.4028/www.scientific.net/AMM.766-767.383

[88]Zhou W, Zuo J, Zhang X, Zhou A. Thermal, electrical, and mechanical properties of hexagonal boron nitride-reinforced epoxy composites. Journal of Composite Materials. 2013;48(20):2517-26. https://doi.org/10.1177/0021998313499953