Influence of nanoparticles on the characters of polymeric composites

R. Vinayagamoorthy¹*, K. S. Subrahmanyam², K. Murali Krishna Murthy³, K. Arun Prajwar⁴, P. Gopinath⁵, M. Sai Lahari⁶ and K. Pruthvi Rangan⁷

¹-⁷ Department of Mechanical Engineering, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Kancheepuram, Tamilnadu - 631561, India.

Email: vin802002@gmail.com

Abstract. The need of structural materials is inevitable for machineries, equipment’s and tools. These materials are mostly made up of metals and polymeric composites and with other materials in rare cases. Polymeric composites nowadays replace almost all materials due to its improved characters and reduced manufacturing costs. The characters of these polymeric composites are improved by reinforcing multiple fibers in it and thus enhances its suitability for different applications. Among the characters of a composites, weight reduction is a vital property that decides the usability of the material in high end applications like aircraft, robots etc. Weight of composites could be enhanced without losing its characters by reinforcing nanoparticles in different forms. Several nanomaterials have been utilized by researchers in various forms and they are proven to be the best in enhancing the characters of the composites. The present research gives a clear picture on the different challenges during the synthesis, fabrication and characterization of nanoparticles reinforced plastic composites.

1. Introduction
Polymeric composites are produced by taking a polymer as the matrix and a fiber as the reinforcement. The matrix gives the structure whereas the reinforcements add the properties to the component [1, 2]. At the earlier stage, man-made fibers have been utilized but later, green fibers taken from nature are used as reinforcing fibers [3-5]. Before using a natural fiber, it must be subjected to several pretreatment techniques in order to remove the unusable matters [6-10]. Polymeric composites are mainly intended for boats and radial fan blades and other components in automotive, aircraft and marine industries [11-14]. Due to the increasing need of polymer-based materials, there is an urge to develop materials without sacrificing the characters. This made the scientists to use nanoparticles in polymeric materials [15-17]. Nanoparticles are made from chemical compounds especially from oxides like zirconium oxide (ZrO₂), hafnium oxide (HfO₂), zinc oxide (ZnO), ferrous oxides (Fe₂O₃ and Fe₃O₄), titanium oxide (TiO₂), aluminium oxide (Al₂O₃) and silicon dioxide (SiO₂). Some polymers adaptable to these nanomaterials are polymethylmethacrylate (PMMA), polyacrylic acid (PAA), polyethylene (PE), polystyrene (PS), acrylic acid etc. Nanomaterials are used in different ways in a polymeric composite. Particles and fillers of nanomaterials are added in the polymer before composite fabrication. Nanoparticles in the form of fibers like carbon nanotubes (CNT) are directly used as
reinforcement as a replacement to commercial fibers during composite fabrication [18, 19]. The other forms of nanomaterials are shown in Figure 1. The influence of nanoparticle in a composite depends upon the size and shape of it and also its characters but majority of research have proved that the addition of nanomaterials enhances the characters of the composite [20, 21]. The present review gives a clear view on the various nanomaterials and their influence on the mechanical characters of the composite materials.

![Figure 1. Different shapes of nanomaterials](image)

2. Carbon based nanoparticles in composites

CNT is found to be one of the vital compounds among the nanomaterials. CNT when mixed as a filler in acrylonitrile butadiene styrene (ABS) matrix is proved to be a good insulator of sound and hence are more apt for sound proofing devices. The composition of CNT in the material has a predominant influence and it is found that a minimum of 15 % of CNT is to be retained in order to achieve optimum sound proofing [22, 23]. CNT is also found to be more suitable for epoxy matrix and the mixing is to be done through ultrasonic probe sonicator. A research on CNT reinforced composites used short fibers of CNT as reinforcement in PMMA matrix. It has been identified that, a fiber length of 10 nm at a composition of 10 % elevated the Youngs modulus and tensile strength as compared to that of the virgin polymeric composite [24, 25]. CNT particles in polymeric composites also elevates the interlaminar shear strength (ILSS) and flexural strength of the composites to a notable extent. In addition, the presence of CNT particles enhances the stability of the composites to retain its mechanical strengths and storage modulus until 200°C. [26, 27]. Graphene is another allotrope of carbon which has almost similar characters like CNT. A research has been made by using graphene nanoparticles and glass as reinforcements in epoxy matrix and reported that, the load bearing ability of the material enhances as a result of graphene addition. The optimum value of graphene is observed as 0.1 % [28]. Like this, many results have been evolved by using carbon nanoparticles. Some of them with their influences on composite characters are presented in Table 1.

| S. No. | Nanoparticles used | Matrix used         | Findings                                                                                                                                   | Reference |
|-------|--------------------|---------------------|-------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 1.    | CNT                | Epoxy               | 0.6 % of CNT inclusion improved the stiffness of the composites by 60 %.                                                                     | 29        |
| 2.    | Carbon and silica particles | Epoxy           | 0.25 % of carbon and 0.25 % of silica in epoxy produced optimum tensile and fatigue performance.                                             | 30        |
| 3.    | Expanded Graphite (EG) | Poly tetrafluoro | Addition of nano-EG enhanced the hardness of the matrix whereas the stress                                                               | 31        |
3. **Natural and nanomaterial reinforced hybrid composites**

Nanoparticles may also be produced from natural fibers like jute, hemp, sisal etc and this could be achieved by using ball milling technique. A research has been made to synthesize jute nanoparticles in size ranging from 10 nm to 30 nm using ball milling and reinforced in to the epoxy matrix to form composites. Thermal properties of the composites have been tested and revealed that, the nanoparticles enhance the crystallization and thermal degradation temperature. In addition, the nanoparticles stabilize the resin molecules and eliminates the occurrence of cracking as a result the storage and loss modulus of the composites and the interfacial adhesion are enhanced [37, 38]. CNT is used as one of the reinforcements in a hybrid composite along with natural fibers such as banana, jute and flax. Investigations on the influence of CNT composition and fiber stacking sequence showed that, a hike in the CNT composition elevates the mechanical strengths of the composite. On the other hand, the stacking sequence also plays a vital role in determining the characters. Among the tested samples, it is observed that a 1 % CNT composition and using the jute layers at the extremities gives optimum mechanical properties to the composite material [18]. In a research, calcium carbonate nanoparticles are deposited on to the bamboo fibers by an ironic solution reaction at various temperatures. The deposited bamboo fibers are then reinforced in polypropylene matrix in the form of structural composites. It is revealed that, a highest absorbance of calcium carbonate is achieved at a temperature of 25°C. Also, it is suggested that the precipitating method is a best method to densify and hydrophobize the natural fiber alleviating the cell wall defects [39, 40].

---

| 4. | CNT | ethylene Ultra-high-weight polyethylene | relaxation time is extended. CNT improves the composite stiffness, impact strength and damping capacity. The developed composites are more suitable for aerospace and naval industries. |
| 5. | CNT | Epoxy | Addition of CNT alleviates the tensile strength and impact strength of the composites. The natural frequency of the composite increases with a hike in CNT content. |
| 6. | Carbon nano fibre (CNF) | Epoxy | Improvement in the tensile modulus and hardness in the CNF reinforced composites as compared to that of the neat resin. |
| 7. | CNF | Epoxy | Inclusion of 16 % CNF in the matrix produced optimum electromagnetic interference shielding effectiveness. CNF is better than CNT, EG and carbon black. |
| 8. | CNT | Epoxy | Mechanical properties such as flexural strength, interlaminar shear strength and tensile strength goes up with an elevation in CNT content until 0.3 %. After 0.4 % of CNT content, the properties decline due to agglomeration and poor wetting of fibers. |
4. Ceramic nanomaterial-based composites
Ceramic materials are majorly used in the form of nanoparticles. In a research, clay and silica are organically synthesized using 3-aminopropyltriethoxysilane by sonication process before using it as a reinforcement in the composite material. Composites have been prepared with epoxy as the matrix and glass as the supporting reinforcement. Wear characters have been studied and reported that, a load and sliding speed showed a lesser debris formation. Also, it is noticed that the presence of nanoparticles alleviates the wear rate of the composites as compared to that of the virgin composite [41, 42]. Aluminium nitride (AlN) and aluminium oxide are a kind of naturally occurring ceramics and have several usages in the ceramic industry. A study has been made to investigate the behaviour of AlN and Al₂O₃ nanoparticles in PEEK matrix composites and revealed that, the microhardness of the composites goes up with an elevation in the fiber loading. In comparison, AlN composites showed an enhanced microhardness than the Al₂O₃ composites [43, 44]. A study on the influence of silica and Si-C₃H₇ treated silica has been made by using polyimide matrix and concluded that, the elevation in the nanoparticle size alleviates the mechanical properties of the composite. On the other hand, when the composite is reinforced with treated silica, the mechanical strengths of the composite goes up to certain extent. It is also identified that, the grafting ratio has a direct impact on the characters such as Youngs modulus, shear modulus and poisson’s ratio [45, 46]. The ratio between degree of polymerization (P) and the degree of polymerization of the grafted bush (N), P/N ratio has also had a predominant influence on the mechanical characters of the composite and this has been identified in a research on nanosilica reinforced on to the polystyrene matrix [47, 48]. Several studies have been to assess the influence of ceramic nanomaterials. Some of them are presented in Table 2.

### Table 2 Influence of ceramic-based nanoparticles on composite characters

| S. No. | Nanoparticles used | Matrix used                          | Findings                                                                 | Reference |
|-------|--------------------|--------------------------------------|--------------------------------------------------------------------------|-----------|
| 1.    | Aluminium oxide    | Epoxy                                | Addition of nanoparticle alleviates the tensile strength and impact strength of the composites. The natural frequency of the composite increases with a hike in nanoparticle content. | 33        |
| 2.    | Silica             | Polyester                            | Residual strength and stiffness of the composites goes up when the silica nanocoating is given to glass fibers. | 49        |
| 3.    | Titania and hydroxyapatite | Poly-lactic-co-glycolic acid | Well dispersed nanoparticles in the matrix enhanced the tensile strength, tensile modulus and compressive modulus of the composites | 50        |
| 4.    | Barium sodium niobite | Polystyrene                          | Improved adhesion between the filler and polymer leading to elevate tensile properties of the composite. | 51        |
| 5.    | Barium titanate, strontium titanate | Poly ε-caprolactone                | Improvement in the mechanical properties as a result of nanoparticles. In addition, nanoparticles elevated the permittivity and reduced the losses in composites. | 52        |
| 6.    | Barium titanate    | Epoxy                                | Dielectric constant and dissipation factor of the composites elevates with the inclusion of nanoparticles. | 53        |
| 7.    | Barium titanate    | Polyvinyl alcohol                    | Dielectric constant goes up with a hike in the ceramic concentration whereas dielectric loss tangent goes down with | 54        |
8. Aluminium oxide and silica Polymethylmethacrylate

Composites with aluminium oxide nanoparticles showed an increased impact strength and fracture toughness as compared to silica reinforced composites.

5. Synthetic nanomaterial-based composites and applications

Processing of nanomaterials are usually done through artificial synthesis of chemicals. Among the several synthetic materials, TiO$_2$ has been utilised as the nanoparticle with a size of 300 nm in epoxy and polyamide matrices during composite preparation. A detailed analysis on the wear performance has been made and it is revealed that, the stress concentration of the fibers in the composite is alleviated and thus there seems to be an enhancement in the wear resistance [56-57]. A mixture of ZrO$_2$ and SiO$_2$ are found to be apt for dental applications when used in combination with matrices based on monomeric di-methacrylate. A comparative study between micro-SiO$_2$ and a mixture of nano ZrO$_2$ and SiO$_2$ particles has been made and showed that, the hardness and reduced modulus are heterogeneous in microfiber composites whereas they are homogeneous in nanofiber composites. Hence, the wear behaviour of nanoparticle composites are superior to the microfiber composites [58, 59]. Magnetic iron oxide (Fe$_3$O$_4$) prepared in the size of 25 nm by co-precipitation of FeCl$_2$ and FeCl$_3$ using sodium hydroxide solution has been utilised as the nanoparticles in epoxy matrix for composite fabrication. Penetration tests have been conducted on the fabricated materials and it has been found that, addition of 5 % nanoparticles improved the resistance to penetration by 9 % in comparison to the composite without nanoparticles [60, 61]. In another research, polymethyl phenyl siloxane is filled with Co$_3$O$_4$ nanoparticles and then reinforced on to poly butyl methacrylate and reported that, after grafting the hydrophilicity of nanoparticles has been alleviated and the hydrophobicity has been elevated. Moreover, it has been concluded that the endothermic characters of the nanoparticle reinforced composites are far better than the virgin composites [62-64]. A research used calcium carbonate nanoparticles as reinforcement in ethylene-propylene-diene rubber during composite formulation and reported that, nanoparticles alleviated the glass transition temperature of the composite to a notable extent in comparison to the microparticles [65, 66]. Like this there several other research works which are primarily made to enhance the characters of the composite in any way and makes it suitable for variety of applications [67, 68]. Nanoparticle based polymer composites finds several applications. The major phenomenon of weight reduction enriches the usage of nanocomposites in aircraft industry. The various possible ways that a nanocomposite could be used in an aircraft is presented in Figure 2.
6. Conclusions
This paper has made a comprehensive survey on various research pertaining to the nanoparticle reinforced plastic composites. Many nanoparticles have been utilized by the researchers and majority of it have produced a positive sign in enhancing the mechanical characters of the composite. Very few researches have produced negative sign but at the same time they are capable of elevating some other physical or chemical characters of the composites. The processing techniques used for a nanomaterial is different for each material and thus the selection synthesis technique is vital as it directly affects the characters of the composite material. A major research work has been done by using carbon in any form as a nanomaterial and all these resulted in elevating the strengths and other physical characters of the composite. Natural fibers on the other hand have also produced superior results in comparison to that of the synthetic material in nano form and thus, natural nano material is apt for polymeric composites. When polymeric composites are used in high temperature applications ceramic nanomaterials are proven to be the best among all nanomaterials.

References
[1] Mahmoud Nassar M A, Ramanathan Arunachalam and Khalid Alzebdeh I 2017 Int. J. Adv. Manuf. Technol. 88 2985.
[2] Vinayagamoorthy R 2017 J. Reinf. Plast. Compos. 36 1577.
[3] Vinayagamoorthy R and Rajeswari N 2014 J. Reinf. Plast. Compos. 33 81.
[4] Vinayagamoorthy R 2019 Polym. Polym. Compos. doi: 10.1177/0967391119883163.
[5] Michael Fuqua A, Shanshan Huo and Chad Ulven A 2012 Polym. Rev. 52 259.
[6] Vinayagamoorthy R, Sivanarasimha S, Vijay Padmanabhan, Vedula Ganesh and Karthikeyan S 2015 Int. J. Appl. Eng. Res. 10 663.
[7] Vinayagamoorthy R 2019 J. Nat. Fiber. doi: 10.1080/15440478.2019.1598916.
[8] Sunil Kumar Ramamoorthy, Mikael Skrifvars and Anders Persson 2014 Polym. Rev. 55 107.
[9] Vinayagamoorthy R, Sivanarasimha S, Vinay Kumar K R and Vijay Padmanabhan 2015 Appl. Mech. Mater. 813 14.
[10] Vinayagamoorthy R and Venkatakoteswararao G 2019 J. Thermoplast. Compos. Mater. doi: 10.1177/0892705719828783.
[11] Rajani Samal K and Giti Sudha Giri 1992 J. Macromol. Sci. Part C: Polym. Rev. 32 55.
[12] Vinayagamoorthy R, Karthikeyan S, Prem Bhargav R S and Rajivalochan T V 2015 Appl. Mech. Mater. 813 101.
[13] Vinayagamoorthy R and Madhavan S 2011 Int. J. Bus. Rev. Manuf. Manage. 1 5.
[14] Vinayagamoorthy R, Mothilal T and Madhavan S 2009 Int. J. Des. Manuf. Technol. 3 63.
[15] Thomas Hanemann and Dorothee Vinga Szabo 2010 Mater. 3 3468.
[16] Vinayagamoorthy R, Saswath Koundinya, S L, Mani Teja G L S N and Kovuru Adithya 2016 Indian J. Sci. Technol. 9 1.
[17] Vinayagamoorthy R 2018 J. Thermoplastic. Compos. Mater. doi: 10.1177/0892705718815529.
[18] Mohan K and Rajmohan T 2017 J. Nat. Fiber. 6 864.
[19] Vinayagamoorthy R, Tumuluri Nikhil Koteshwar, Vajhala Venu Madhav, Twarakavi Karthik Sai and Vikas Konda 2019 Mater. Today: Proc. 27 1.
[20] Vinayagamoorthy R, Vikas Konda, Parikshit Tonge, Tumuluri Nikhil Koteshwar and Premkumar M 2019 Mater. Today: Proc. 67 567.
[21] Zhanhu Guo, Ta Kim Y, Kenny Lei, Tony Pereira, Jonathan Sugar G and Thomas Hahn H 2008 Compos. Sci. Technol. 68 164.
[22] Vinayagamoorthy R, Ankur Shama, Vignesh Iyer and Navneeth G 2019 Adv. Manuf. Processes., Lect. Notes Mech. Eng. 48 521.
[23] Jae-Chul Lee, Young-Sun Hong, Ri-Guang Nan, Moon-Kyu Jang, Caroline Lee S, Sung-Hoon Ahn, and Yeon-Jun Kang 2008 J. Mech. Sci. Technol. 22 1468.
[24] Rajmohan T, Vinayagamoorthy R and Mohan K 2018 J. Thermoplastic. Compos. Mater. doi: 10.1177/0892705718796541.
[25] Behrouz Arash, Harold Park S and Timon Rabczuk 2015 Compos. Struct. 134 981.
[26] Vinayagamoorthy R, Rajeswari N and Balasubramanian K 2014 Jordan J. Mech. Ind. Eng. 8 385.
[27] Ming-Chuen Yip, Yi-Chieh Lin and Chung-Lin Wu 2011 Polym. Polym. Compos. 19 131.
[28] Tuncer C and Canyuri OE 2019 Acta Physica Polonica A. 135 752.
[29] Abdullah Algarni, Numan Salah, Mostefa Bourchak, Asim Jilani, Ahmed Alshahrze and Mahmoud Nadim Nahas 2016 J. Compos. Mater. 51 2675.
[30] Megahed M, Megahed AA and Agwa MA 2018 J. Indust. Tex. 49 181.
[31] Yanhong Yana, Zhining Jiaa and Yulin Yang 2011 Procedia Environ. Sci. 10 929.
[32] Maksim Kireitseu, David Hui and Geoffrey Tomlinson 2008 Compos. Part B: Eng. 39 128.
[33] Mohammed SM, Gamil M, Mohammed SS, Mahmoud TS and El-Kady MEY 2017 Nanosci. Nanotechnol. 11 1.
[34] Lee H, Mall S, Nalladega V, Sathish S, Roy A and Lafdi K 2006 Polm. Polm. Compos. 14 549.
[35] Moumita Ray, Jinu Jacob George, Ajay Chakraborty and Anil Bhowmick K 2010 Polm. Polm. Compos. 18 59.
[36] Salam MBA, Hosur MV, Jahan N, Rahman MM and Jeelani S 2013 Polm. Polm. Compos. 21 495.
[37] Vinayagamoorthy R 2018 J. Reinf. Plast. Compos. 37 49.
[38] Padal KTB, Srikiran S and Surya Nagendra P All India Manuf. Technol. Des. Res. Conf. IIT Guwahati, 12 Dec 2014.
[39] Vinayagamoorthy R 2017 Mater. Manuf. Processes. 32 645.
[40] Gao Jie, Wang Ge, Cheng Hai-tao and Sheldon Q Shi 55th Int. Conven. Soc. Wood Sci. Technol. Beijing, 27-31 Aug 2012.
[41] Vinayagamoorthy R 2019 J. Nat. Fib. 16 163.
[42] Lingaraju D, Ramji K, Pramila Devi M and Rajya Lakshmi U 2011 Bull. Mater. Sci. 34 705.
[43] Vinayagamoorthy R, Rajeswari N, Vijayshankar S and Balasubramanian K 2014 Int. Rev. Mech. Eng. 8 952.
[44] Goyal RK, Tiari AN and Negi YS 2008 Mater. Sci. Eng. A 491 230.
[45] Kannan P, Balasubramanian K and Vinayagamoorthy R 2015 Int. Rev. Mech. Eng. 9 536.
[46] Hui Zhang and Jiachu Xu 2016 J. Chem. Pharm. Res. 8 39.
[47] Vinayagamoorthy R, Rajeswari N and Karthikeyan S 2015 Appl. Mech. Mater. 766-767 812.
[48] Marissa Giovino, Julia Pribyl, Brian Benicewicz, Ronald Bucinell and Linda Schadler 2019 Nanocompos. doi: 10.1080/20550324.2018.1560988.
[49] Yongchao Zhang and Changwen Mi 2019 *J. Appl. Polym. Sci.* **48652** 1.
[50] Huinan Liu and Thomas Webster J 2010 *Int. J. Nanomedicine* **5** 299.
[51] Abraham R, Thomas SP, Kuryan S, sac J, Varughese KT and Thomas S 2009 *eXPRESS Polym. Lett.* **3** 177.
[52] Amrit Bagchi, Sai Rama Krishna Meka, Badari Narayana Rao and Kaushik Chatterjee 2014 *Nanotechnol.* **25** 485101.
[53] Pratap A, Joshi NJ, Rakshit PB, Grewal GS and Shrinet V 2013 *Int. J. Modern Phy: Conf. Ser.* **22** 1.
[54] Beena P and Jayanna HS 2019 *Polym. Polym. Compos.* **27** 619.
[55] Ahmed Alhareb O, Hazizan Md. Akil and Zainal Arafin Ahmad 2016 *Polym. Polym. Compos.* **24** 71.
[56] Venkatakoteswara Rao G, Vinayagamoorthy R, Abinesh K, Sudharsan M, Ponmeganathan S and Deepak Kumar LS 2020 *Adv. Mater. Manuf. Eng., Lect. Notes Mech. Eng.* 533.
[57] Li Chang and Klaus Friedrich 2010 *Tribol. Int.* **43** 2355.
[58] Vinayagamoorthy R, Rajeswari N, Vijayshankar S, Vivekanandan M, Sri Rama Murthy Bellala and Venkata Subramaniam KR 2014 *Procedia Mater. Sci.* **5** 2075.
[59] Devaprakasam D, Hatton PV, Möbus G and Inkson BJ 2007 *J. Phy: Conf. Ser.* **126** 012057.
[60] Vinayagamoorthy R, Shubham Kumar, Suraj Kumar, Mote Sai Sharan, Afzal GMD and Rajamurugan TV 2020 *Adv. Mater. Manuf. Eng., Lect. Notes Mech. Eng.* 43.
[61] Hany Fouda, Khalid Ghith and Lin Guo 2017 *MATEC Web Conf.* **88** 01002.
[62] Vinayagamoorthy R, Manoj I V, Narendra Kumar G, Sai Chand I, Sai Charan Kumar G V and Suneel Kumar K 2018 *J. Mech. Sci. Technol.* **32** 2011.
[63] Vinayagamoorthy R and Rajmohan T 2018 *J. Reinf. Plast. Compos.* **37** 1037.
[64] Sun JT, Huang YD, Cao HL and Gong GF 2004 *Polym. Polym. Compos.* **12** 739.
[65] Vinayagamoorthy R, Manoj IV, Narendra Kumar G, Sai Chand I, Sai Charan Kumar GV and Suneel Kumar K 2018 *IOP Conf. Ser: Mater. Sci. Eng.* **390** 012029.
[66] Yabin Zhou, Shifeng Wang, Yong Zhang and Yinxi Zhang 2006 *Polym. Polym. Compos.* **14** 527.
[67] Ambiga K, Annadurai R and Vinayagamoorthy R 2016 *Indian J. Sci. Technol.* **9** 1.
[68] Vinayagamoorthy R, Kanakadandi Guru Subramanyam, Tuduru Nikhil Kumar and Yerasi Harshavardhan Reddy 2016 *Indian J. Sci. Technol.* **9** 1.