American Journal of Polymer Science & Engineering
http://www.ivyunion.org/index.php/ajpse/

Review Article

Amalgamation of Nanodiamond and Epoxy

Ayesha Kausar[1]*

[1] Nanoscience and Technology Department, National Centre For Physics, Islamabad, Pakistan

Abstract

Nanoscale diamond particles are known as nanodiamond (ND). Nanodiamond has attracted much attention of the polymeric composite community. Owing to its superior properties, ND holds great potential to improve tribological characteristics of the composites. In epoxy/nanodiamond nanocomposite, large surface to volume ratio of ND results in dramatic increase in volume of inter-phase, i.e. polymer volume which is close enough to nanodiamond. This, in turn, allows nanodiamond to exert significant impact on epoxy properties even at low concentrations. It is critically important to have physical/covalent bond at epoxy/ND interface from nanoparticle surface to the macromolecules of the matrix. Mechanical properties, thermal stability and electrical conductivity of the covalently compatiblized epoxy/ND composite have been found better than neat epoxy matrices and compatible composites. Epoxy/ND composite has huge range of technical applications ranging from biomedical—to—electronics—to—aerospace.

Keywords: Epoxy; Nanodiamond; Interface; Nanocomposite; Application

Received: January 25, 2017; **Accepted**: February 18, 2017; **Published**: March 14, 2017

Competing Interests: The authors have declared that no competing interests exist.

***Correspondence to:** Ayesha Kausar, Nanoscience and Technology Department, National Centre For Physics, Islamabad, Pakistan

E-mail: asheesgreat@yahoo.com

1. Introduction

Nanodiamond (ND) forms a significant class of nanomaterials. ND is about 5 nm in diameter. Nanodiamond not only has exceptional features of diamonds such as hardness, stiffness, chemical stability, and strength, but also has the significance of nanomaterials such as large surface area and other physical and structural properties [1]. In 1963, nanodiamond was discovered in explosive mixtures in immense concentration. The mass production of ND was started in 1990s [2]. Nanodiamond covers miscellaneous areas of research. A very significant use is found in polymer/nanodiamond composite. ND possesses marvellous physical and chemical properties relative to the conventional constituents. Different methods have been used to prepare high performance polymer/ND composite [3-5]. The main focus of these methods is to achieve efficient dispersion of detonation nanodiamond particles in amorphous thermoplastic/thermoset matrices. For estimation of polymer/nanodiamond properties, various microscopic and physical techniques have been used. In polymer/nanodiamond composite, mechanical properties, thermal features, and large surface to volume ratios are important parameters. ND reinforcement in matrices has led to ultra-high stiffness and hardness of polymer/nanodiamond nanomaterial [6-8]. The mechanical properties of polymers reinforced with nanodiamond nanofiller have been studied. Even at very small content (~1 wt.%), mechanical properties have been increased up to 100 % [9, 10]. Both physical as well as chemical bondings have been observed in these nanocomposites. However, the exact mechanism of reinforcement in the polymer/ND composite is still unknown. The synergy between the nanofiller content and polymer properties has also been stressed. Polymer/nanodiamond composite have been employed in several structural applications, biomedical, magnetic sensors, etc. In this article, a brief but comprehensive coverage of nanodiamond—to—polymer/nanodiamond materials has been conversed.

2. Nanodiamond

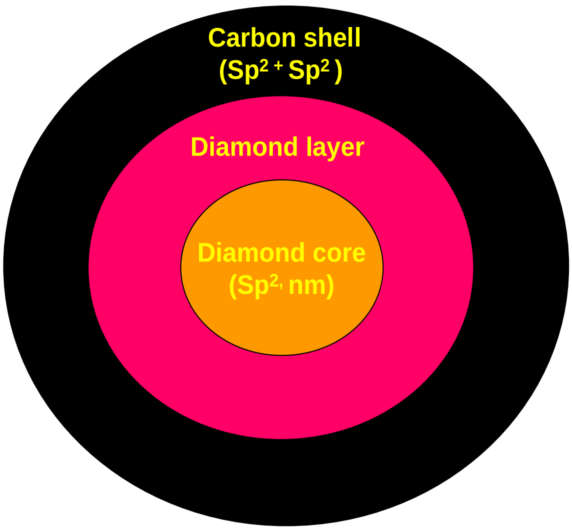

Fig. 1 Nanodiamond structure

Nanodiamond (ND) is a member of nanocarbon family comprising diamondoids, fullerenes, tubes, onions, horns, cones, rods, and several other forms [11-13]. The electronic configuration of carbon is $1s^2$, $2s^2$, $2p^2$. In graphite, carbon atom has sp^2 hybridization to form two dimensional planar hexagonal structure. On the other hand, tetrahedral structure of diamond is formed by sp^3 hybridization. The carbon layer stacking form modified face centered cubic structure [14]. The structure of ND particle consists of a central part of diamond core made up of sp^3 hybridized carbon, core is covered by shell of sp^2 hybridized carbon, and outer surface with functional groups formed by carbon atoms (Fig. 1) [15]. Initial studies on ND were performed in 1960s. However, ND was unknown to the world till 1980s. In late 1990s, number of significant breakthroughs led to immense attention towards nanodiamond in materials technology. The most commonly used method for the production of nanodiamond (large scale) is the detonation synthesis. Detonation of carbon containing explosive may produce small sized particles of ~4-5 nm. Nanodiamond usually has narrow size distribution and facile surface functionalization capability. ND surface comprises various hydrocarbon functional groups such as carboxylic, ether, oxiran, and carbonyl groups [16]. Consequently, ND has intrinsic hydrophilic surface to be employed in biomedical applications. ND is excellent contender for surface functionalization Due to the nano-size, large and open surface area (300-500 m^2/g), and characteristics for purification with oxidizing agents [17]. A simple reaction of epoxide monomer with acid functional nanodiamond is given in Fig. 2.

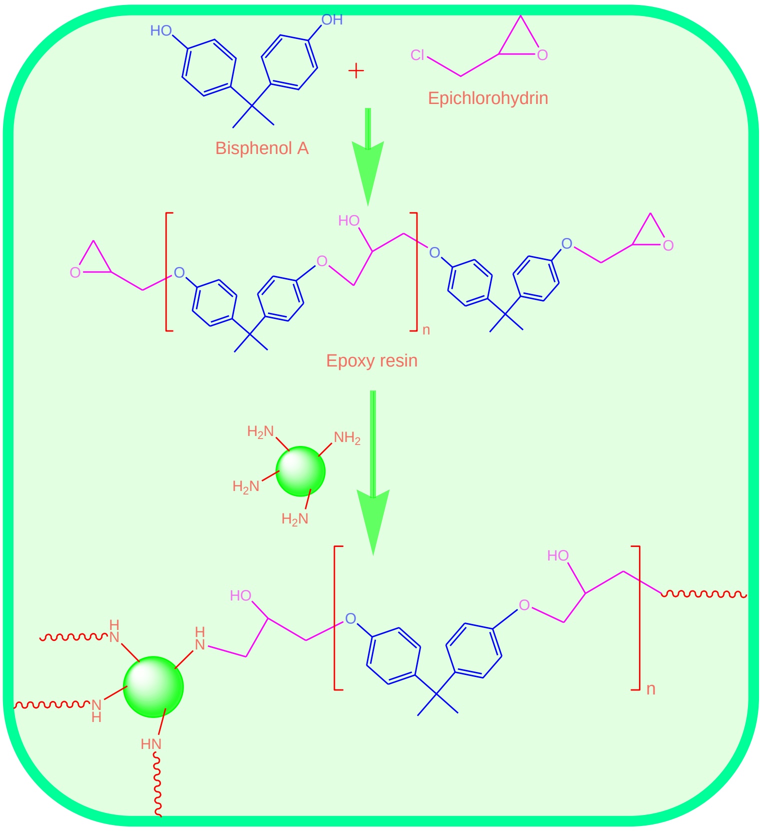

Fig. 2 Chemical reaction between epoxy and functional nanodiamond.

3. Polymer and nanodiamond composite

Nanodiamond particles endow superior hardness, Young's modulus, electrical resistivity, high thermal conductivity, chemical stability, and biocompatibility to polymer nanocomposites. Consequently, excellent features make ND an excellent candidate for polymer reinforcement. The influence of ND on mechanical features of polymers and rubbers has been investigated [18, 19]. Polyvinyl alcohol (PVA) and nanodiamond composite have been studied [20]. The matrix was reinforced with up to 7 wt.% ND. The stiffness and strength of PVA/ND were found to increase, however ductility was decreased with large ND concentration. Polyamide and ND composites were also reported. There was considerable increase in the Young's modulus and hardness of ~20wt. % ND loaded polyamide fibers [21]. Properties of polyacrylonitrile and polyamide 11 nanofibers have also been improved with the addition of ND content. Poly(methyl methacrylate) (PMMA) and modified ND have been used in for improvement of mechanical properties in dental implants. Polycarbonate (PC) has also been reinforced with pure and functionalized ND. PolyLactic acid composites has also shown improved storage modulus, tensile modulus, and the tensile strength with 5 wt.% ND loading [22]. Similarly, several other type of polymer/ND composite has been reported [23-32].

4. Epoxy/nanodiamond amalgamation

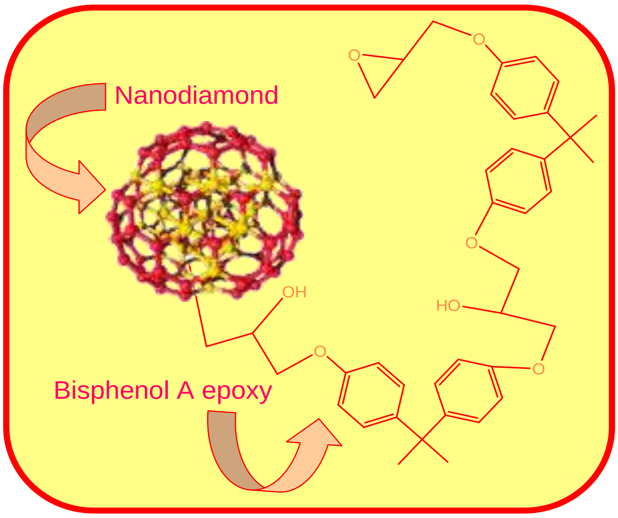

Fig. 3 Covalent interaction between epoxy chains and nanodiamond.

A common thermosetting polymer is epoxy, which is used as matrix material for composites in building materials, adhesives, composites, laminates, and coatings due to low cost, adhesion properties, and outstanding mechanical and thermal resistance. Epoxy resins are also known as polyepoxides. These are reactive prepolymers/polymers with epoxide groups. Epoxy resins may be reacted or cross-linked using various catalysts, diamines, polyfunctional amines, multi-functional acids, and alcohols. Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer. Several nanofillers have been investigated to reinforce epoxy systems. Polyamide, poly(vinyl alcohol), polyisoprene, and poly(L-lactic acid) composites have been reported with nanodiamond. So, it sis mostly reinforced in thermoplastic matrices [33]. Epoxy/ND composites have been prepared using various routes such as simple solution phase method, melt mixing, in-situ technique, electrospinninmg, and several other methods. Epoxy/ND composites with nanofiller loading demonstrated significant increase in glass transition temperature and other physical properties. On the other hand, the composites of ND with thermosetting polymers have been less studied. Mechanical behaviour of epoxy/ND composites has been studied. Storage modulus, Young's modulus, and hardness have been investigated for epoxy/ND nanocomposite [34]. Enhanced mechanical features have been observed at low ND content. Epoxy/ND composites have been considered significant for engineering applications. The curing of epoxy has been achieved by mixing with various hardeners and cross linkers [35]. Thermal conductivity of epoxy/nanodiamond composites with nanodiamond concentration (0-25 vol.%) have also been widely studied in addition to the mechanical properties [36]. The nanodiamond may interact chemically with the epoxy chain as shown in Fig. 3.

Epoxy/nanodiamond derivatives have also been synthesized using grafting epoxy monomers onto the surface of nanodiamond. The materials have been characterized by thermogravimetric analysis (TGA) and Fourier transform infra red (FTIR) spectroscopy. The ratio of grafted epoxy groups was determined by TGA. The epoxy functionalization of nanodiamond material enables variety of advanced engineering and biomedical applications. Amine-functional ND-NH_2 has also been reacted with the epoxy resin. The formation of strong covalent epoxy/ND interface was identified by differential scanning calorimetry (DSC). Tetrahydrofuran (THF) was used as solvent. ND-NH_2-epoxy composites with uniformly dispersed particles exhibited improved Young's modulus for the compatible nanocomposite [37, 38]. Similarly, extensive tribological studies have been performed on epoxy/ND nanocomposite. The materials showed improved properties at very low nanodiamond content. Addition of only 0.1 wt.% ND may decrease the coefficient of friction and the wear rate, however increase the tensile strength, toughness and hardness of the material.

5. Significance of epoxy/nanodiamond composite

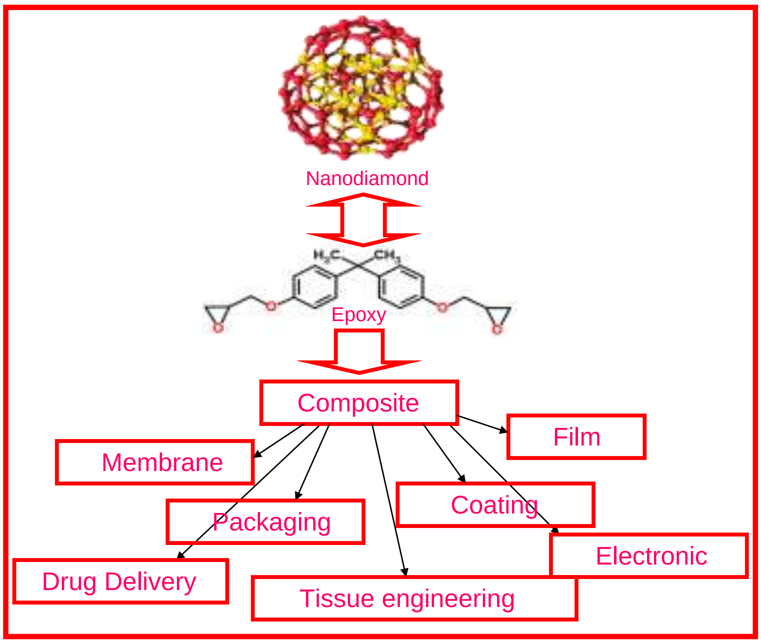

Fig. 4 Applications of epoxy/ND nanocomposite.

Applications of multifunctional epoxy/ND have been focused (Fig. 4). Epoxy/ND composites exhibit unique combination of properties for electronics, packaging, membranes, and biomedical applications such as tissue engineering scaffolds, drug delivery, and biomedical polymer devices with ND. Electromagnetic compatibility is essential in functioning of electrical devices. Moreover, it is important to shield the electrical devices (integrated circuits, processors, and equipments) against electromagnetic interference. Consequently, epoxy/ND nanocomposites have been used as shielding materials. Epoxy/ND has excellent electromagnetic absorption features due to high electronic conductivity and high defective inner shells [39]. Thermal conductivity and mechanical features of nanodiamond strengthened epoxy matrix composites have also been studied [40]. Young's modulus and hardness of these composites were found to be improved up to several folds [41]. The bonding between epoxy and ND particles may result in enhanced thermal conductivity of these composites. However, agglomeration in epoxy/ND composites may cause damage to efficient hardness of the material [42, 43]. The properties were found better than the other polymer/carbon nanofiller composite [44-50].

6. Conclusion

Nanodiamond presents several advantages to epoxy nanocomposites. Foremost compensations of nanodiamonds are small and uniform size, nearly spherical shape, large and accessible surface area, and superior mechanical, electric, optical, and thermal properties. In epoxy matrix, these nanoparticles maximize interactions i.e. the interphase formation due to tailorable surface chemistry. Spherical shape of ND maximizes the interphase volume per nanoparticle volume, and so contributes to improved mechanical properties of the nanocomposite. At low concentration, small nanodiamond particle size minimizes the interparticle distance, and develops close contact between the nanoparticles. This results in higher thermal conductivity and better mechanical strength of the resulting epoxy nanocomposite. Type of ND, surface modification, concentration, dispersion, and fabrication technique effectively influences the epoxy/ND composites.

Reference

1. Kausar A, Ashraf R, Siddiq M. Polymer/nanodiamond composites in Li-ion batteries: A review. ***Polym-Plast Technol Engineer.*** 2014, 53:550-563
2. Ashraf R, Kausar A, Siddiq M. High-performance polymer/nanodiamond composites: synthesis and properties. ***Iran Polym J.*** 2014, 23:531-545
3. Rosenholm JM, Vlasov II, Burikov SA, Dolenko TA, Shenderova OA. Nanodiamond-Based composite structures for biomedical imaging and drug delivery. ***J Nanosci Nanotechnol.*** 2015, 15:959-971
4. Jabeen S, Kausar A, Muhammad B, Gul S, Farooq M. A review on polymeric nanocomposites of nanodiamond, carbon nanotube, and nanobifiller: Structure, preparation and properties. ***Polym-Plast Technol Engineer.*** 2015, 54:1379-1409
5. Ashraf R, Kausar A, Siddiq M. Preparation and properties of multilayered polymer/nanodiamond composites via an in situ technique. ***J Polym Engineer.*** 2014, 34:415-429
6. Attia NF, Rao JP, Geckeler KE. Nanodiamond–polymer nanoparticle composites and their thin films. ***J Nanopart Res.*** 2014, 16:2361
7. Khan DM, Kausar A, Salman SM. Exploitation of Nanobifiller in Polymer/Graphene Oxide–Carbon Nanotube, Polymer/Graphene Oxide–Nanodiamond, and Polymer/Graphene Oxide–Montmorillonite Composite: A Review. ***Polym-Plast Technol Engineer.*** 2016, 55:744-768
8. Ashraf R, Kausar A, Siddiq M. Preparation and properties of layered carbon nanotube/polyazopyridine/nanodiamond composites. ***J Plast Film Sheet.*** 2014, 30:412-434

9. Kausar A. Nanodiamond/mwcnt-based polymeric nanofiber reinforced poly (bisphenol a-co-epichlorohydrin). ***Malaysian Polym J.*** 2015, 10:23-32
10. Kausar A. Properties of Sol-gel Coated Fibers of Polyamide 6/12/Polyvinylpyrrolidone/Nanodiamond. ***Int J Mater Chem.*** 2015, 5:91-95
11. Danilenko, V. V. On the history of the discovery of nanodiamond synthesis. ***Phys Solid Stat.*** 2004, 46:595-599
12. Rao CNR, Satishkumar BC, Govindaraj A, Nat M. Nanotubes. ***Chem Phys Chem.*** 2001, 2:78-105
13. Osawa E. Single-nano buckydiamond particles: Synthesis strategies, characterization methodologies and emerging applications. In: Ho, D. ed. Nanodiamond-applications in biology and nanoscale medicine. New York, 2010, 1:1-33
14. Jabeen S, Kausar A, Muhammad B, Gul S, Farooq M. A Review on Polymeric Nanocomposites of Nanodiamond, Carbon Nanotube, and Nanobifiller: Structure, Preparation and Properties. ***Polym Plast Technol Eng.*** 2015, 54:1379-1409
15. Liu X, Pichler T, Knupfer M, Golden M S, Fink J, Kataura H, Achiba Y. Detailed analysis of the mean diameter and diameter distribution of single-wall carbon nanotubes from their optical response. ***Phys Rev B.*** 2002, 66:045411
16. Work W J, Horie K, Hess M, Stepto R F T. Definition of terms related to polymer blends, composites, and multiphase polymeric materials (IUPAC Recommendations 2004). ***Pure. Appl. Chem.*** 2004, 76:1985-2007
17. Shenderova O A, Zhirnov V V, Brenner D W. Carbon nanostructures. ***Critical Rev Sol Stat Mater Sci.*** 2002, 27:227-356
18. Li L, Davidson J L, Lukehart C M. Surface functionalization of nanodiamond particles via atom transfer radical polymerization. ***Carbon.*** 2006, 44:2308-2315
19. Dolmatov V Y. Detonation-synthesis nanodiamonds: synthesis, structure, properties and applications. ***Russ Chem Rev.*** 2007, 76:339
20. Kurkin T S, Ozerin A N, Kechekyan A S, Ozerina L A, Obolonkova E S, Beshenko M A, Dolmatov V Y. Structure of oriented fibers based on poly(vinyl alcohol) modified by detonation nanodiamonds. ***Polym Sci Series A.*** 2008, 50:43-50
21. Behler K D, Stravato A, Mochalin V, Korneva G, Yushin G, Gogotsi Y. Nanodiamond-polymer composite fibers and coatings. ***ACS nano.*** 2009, 3:363-369
22. Mochalin VN, Gogotsi Y. Nanodiamond–polymer composites. ***Diam Relat Mater.*** 2015, 58:161-171
23. Ullah M, Kausar A, Siddiq M, Subhan M, Abid Zia M. Reinforcing effects of modified nanodiamonds on the physical properties of polymer-based nanocomposites: A review. ***Polym Plast Technol Eng.*** 2015, 54:861-879
24. Kausar A. Formation and properties of poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate)/polystyrene composites reinforced with graphene oxide-nanodiamond. ***Am J Polym Sci***. 2014, 4:54-62
25. Kausar A, Ashraf R. Electrospun, non-woven, nanofibrous membranes prepared from nano-diamond and multi-walled carbon nanotube-filled poly (azo-pyridine) and epoxy composites reinforced with these membranes. ***J Plast Film Sheet.*** 2014, 30:369-387
26. Kausar A. Thermal and Rheological Properties of Waterborne Polyurethane/Nanodiamond Composite. ***Nanoscience and Nanotechnology.*** 2016, 6:6-10
27. Kausar A. Effect of Sol-gel Coating on Microscopic, Thermal and Water Absorption Behavior of Aramid/Nylon 6/6/Nanodiamond-based Fibers. ***Am J Curr Org Chem.*** 2015, 1:60-68

28. Kausar A. Mechanical and Thermal Properties of Polyamide 1010 Composites Filled with Nanodiamond/Graphitized Carbon Black Nanoparticles. ***Am J Polym Sci*. *Eng.*** 2015, 3:161-171
29. Kausar A. Polyaniline Composites with Nanodiamond, Carbon nanotube and Silver Nanoparticle: Preparation and Properties. ***Am J Polym Sci*. *Eng.*** 2015, 3:149-160
30. Kausar A. Poly (bisphenol A-co-epichlorohydrin) and Nanodiamonds/Poly (azo-pyridine)/Polyamide/Multi-walled Carbon Nanotube-based Nanofiber Nanocomposites. ***Am J Polym Sci*. *Eng.*** 2014, 2:35-50
31. Kausar A. A Study on Waterborne Polyurethane Coated Polyamide 11 Fiber and Composite Fiber with Nanodiamond. ***Int J Mater Chem.*** 2015, 5:101-105
32. Kausar A. Design and Study of Epoxy Composites based on Polycaprolactone and Nanodiamond Functionalized Carbon Fibers. ***Am J Polym Sci*. *Eng.*** 2015, 3:50-60
33. Špitalský Z, Kromka A, Matějka L, Černoch P, Kovářová J, Kotek J, Šlouf M. Effect of nanodiamond particles on properties of epoxy composites. ***Adv Compos Lett.*** 2008, 17:29-34
34. Stravato A, Knight R, Mochalin V, Picardi S C. HVOF-sprayed nylon-11+nanodiamond composite coatings: production & characterization. ***J Therm Spray Technol.*** 2008, 17:812-817
35. Cadek M, Coleman J N, Barron V, Hedicke K, Blau WJ. Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites. ***Appl Phys Lett.*** 2002, 81:5123-5125
36. Neitzel I, Mochalin V, Knoke I, Palmese G R, Gogotsi Y. Mechanical properties of epoxy composites with high contents of nanodiamond. ***Compos Sci technol*.** 2011, 71:710-716
37. Kausar A. Role of Thermosetting Polymer in Structural Composite. ***Am J Polym Sci Engineer.*** 2017, 5:1-2
38. Raman V I, Palmese G R. Influence of tetrahydrofuran on epoxy−amine polymerization. ***Macromolecules*** 2005, 38:6923-6930
39. Gavrilov NN, Okotrub AV, Bulusheva LG, Sedelnikova OV, Yushina IV, Kuznetsov VL. Dielectric properties of polystyrene/ onion-like carbon composites in frequency range of 0.5–500 kHz. ***Compos Sci Technol.*** 2010, 70:719-724
40. Ullah M, Kausar A, Siddiq M, Subhan M, Abid Zia M. Reinforcing Effects of Modified Nanodiamonds on the Physical Properties of Polymer-Based Nanocomposites: A Review. ***Polym Plast Technol Eng.*** 2015, 54:861-879
41. Monteiro S N, de Menezes G W, Bobrovnitchii G S, Skury A L D, Rodriguez R J S, d'Almeida J R M. Structure and mechanical properties of composites with diamond particles dispersed into modified epoxy matrix. ***Diamond Relat. Mater*.** 2007, 16:974-977
42. Efremov VP, Zakatilova EI. The analysis of thermal stability of detonation nanodiamond. ***Journal of Physics: Conference Series*** 2016, 774:012014
43. Prasad KE, Das B, Maitra U, Ramamurty U, Rao CN. Extraordinary synergy in the mechanical properties of polymer matrix composites reinforced with 2 nanocarbons. ***Proceedings of the National Academy of Sciences.*** 2009, 106:13186-13189
44. Akram Z, Kausar A, Siddiq M. Review on polymer/carbon nanotube composite focusing polystyrene microsphere and polystyrene microsphere/modified CNT composite: preparation, properties, and significance. . ***Polym-Plast Technol Engineer.*** 2016, 55:582-603
45. Kausar A, Ur Rahman A. Effect of graphene nanoplatelet addition on properties of thermo-responsive shape memory polyurethane-based nanocomposite. ***Full Nanotub Carb Nanostruct.*** 2016, 24:235-242

46. Ahmed N, Kausar A, Muhammad B. Advances in shape memory polyurethanes and composites: A review. ***Polym-Plast Technol Engineer.*** 2015, 54:1410-1423
47. Nasir A, Kausar A, Younus A. Novel hybrids of polystyrene nanoparticles and silica nanoparticles-grafted-graphite via modified technique. . ***Polym-Plast Technol Engineer.*** 2015, 54:1122-1134
48. Kausar A, Rafique I, Muhammad B. Review of Applications of Polymer/Carbon Nanotubes and Epoxy/CNT Composites. ***Polym-Plast Technol Engineer.*** 2016, 55:1167-1191
49. Shah R, Kausar A, Muhammad B. Characterization and Properties of Poly (methyl methacrylate)/Graphene, Poly (methyl methacrylate)/Graphene oxide and Poly (methyl methacrylate)/p-Phenylenediamine-Graphene Oxide Nanocomposites. ***Polym-Plast Technol Engineer.*** 2015, 54:1334-1342
50. Kausar A, Rafique I, Anwar Z, Muhammad B. Perspectives of epoxy/graphene oxide composite: Significant features and technical applications. ***Polym-Plast Technol Engineer.*** 2016, 55:704-722