NanoWorld Journal

https://doi.org/10.17756/nwj.2019-063

Review Article | Open Access

Strategies in Polymeric Nanoparticles and Hybrid Polymer Nanoparticles

Ayesha Kausar*

National University of Sciences and Technology, Islamabad, Pakistan

***Correspondence to:**
Dr. Ayesha Kausar, PhD
National University of Sciences and Technology
Islamabad, Pakistan
E-mail: asheesgreat@yahoo.com

Received: November 26, 2018
Accepted: January 21, 2019
Published: January 23, 2019

Citation: Kausar A. 2019. Strategies in Polymeric Nanoparticles and Hybrid Polymer Nanoparticles. *NanoWorld J* 5(1): 1-5.

Published by United Scientific Group

Abstract

Polymer nanoparticles have gained significant research interest in increasing number of fields. Various techniques have been used for the synthesis of polymeric nanoparticles including polymerization of monomers as well as dispersion or processing of the synthesized polymers. While performing nanoparticle synthesis, the resulting particle size, distribution, cost, and end use must be considered beforehand. In addition to polymeric nanoparticles, certain hybrid polymeric nanoparticles have been prepared. The hybrid polymeric nanoparticles include the combination of polymer nanoparticles with other organic or inorganic particles such as carbon nanotube, graphene, graphene oxide, carbon black, silica, zinc, nickel, and several metal oxide nanoparticles. This review actually covers the basics and strategies used for the design of polymer nanoparticles and hybrid polymeric nanoparticles. In future, several crucial parameters must be identified and improved to design these nanoparticles to attain desired properties for high performance applications.

Keywords

Polymer, Nanoparticles, Hybrid, Polymerization, Application

Introduction

Although, the arena of polymer nanoparticles is new, it is quickly growing and playing an essential role in wide spectrum of applications ranging from electronics, devices, and biomedical to environmental technology [1, 2]. The term polymeric nanoparticle is collectively used for any type of polymer nanoparticle, nanospheres, nanoellipsoids, or other similar nanostructures. The advantageous properties and applications of polymeric nanoparticles can be obtained and optimized using various preparation techniques. Polymeric nanoparticles can be prepared using as prepared polymers or through polymerization of the desired monomers. Techniques such as evaporation, precipitation, osmosis, salting out, emulsion, and interfacial polymerization have been used for the preparation of polymeric nanoparticles [3-5]. The monomer polymerizations through emulsion, micro-emulsion, and mini-emulsion are also popular. Thus, these nanoparticles can be prepared using polymers and copolymers along with different solvents and stabilizers. There have been continuous search efforts for synthesizing polymeric nanoparticles with optimum properties using suitable stabilizing agent and solvent system. Key properties of polymer nanoparticles depend on particle size and the particle size distribution. Hybrid nanoparticles have been prepared using polymer nanoparticles and inorganic nanoparticles [6-10]. Efficient hybrid nanoparticle interfacial adhesion and uniform dispersion may lead to transparent films, coatings, and membranes. However, the fundamental knowledge about the processes in the preparation of hybrid polymer nanoparticles is still limited. The control of size, distribution, and morphology of hybrid nanoparticles are not also fully understood. This review article examines unique chemical and physical aspects of polymer-based nanoparticles. It covers different preparation techniques for polymeric nanoparticles and insists parameter control such as particle size, particle size distribution, surface area, etc. Future direction and opportunities for the development of new polymeric and hybrid nanoparticles have also been portrayed. Exploration of structure-property relationship of polymeric nanoparticles is challenges to open new frontier of these materials.

Polymeric Nanoparticles

Nanoparticles can be defined as solid or colloidal particles having size in the range 10-100 nm [11]. Polymer nanoparticles are usually nanospheres, nanocapsules, or oval nanoparticles [12]. The organic molecules or inorganic nanoparticles can be adsorbed on nanoparticle surface or encapsulated in the particles to form a core-shell structure [13]. The size and shape of nanoparticles are of course essential to attain improved material properties for various applications such as optics, catalysis, electronics, etc. The nanoparticle size, size distribution, surface area, and homogeneity are still challenging. Polymer nanoparticles have been used as building blocks to create mesoscale assemblies. The enhanced inter-particle interactions and perfect geometric shape are essential to develop self-assembled ordered mesoscale structure. The polymer nanoparticle assemblies have been used instead of inorganic nanoparticles. Different types of polymers have been used to form polymeric nanoparticles. Variation in polymer architecture and surface functionalization may affect the inter-particle interactions and final nanoparticle properties.

Processing of Polymeric Nanoparticles

Polymeric nanoparticles have been prepared using range of facile techniques [14]. Figure 1 shows the schematic for the preparation of polymer nanoparticles from monomers. Polymer can be directly converted to polymeric nanoparticles using different techniques such as evaporation, precipitation, salting out, dialysis, supercritical fluid technology, etc. On the other hand, monomers can be *in situ* polymerized through emulsion, interfacial, and dispersion methods. The polymerization of monomers through micro-emulsion, mini-emulsion, and free emulsion have found success. Figure 2 shows osmosis method for the preparation of polymeric nanoparticles. As the name osmosis indicates, it uses a semipermeable membrane as physical barrier to the polymer solution [15]. The membrane allows passive transport of solvent molecules to control the mixing of polymer solution with non-solvent.

Figure 3 shows the expansion of supercritical solution in liquid solvent [16]. The nano-sized particles were attained through the suppression of particle growth in expansion jet. The nanoparticles were collected in solvent, and can be dried through solvent evaporation. Figure 4 shows the emulsion polymerization method utilizing solvent, monomer, stabilizer, and surfactant/initiator. The difference between the emulsion polymerization and mini-emulsion polymerization is basically the use of low molecular weight compound as stabilizer. Mini-emulsion polymerization needs high-shear to attain steady state. The emulsion method may produce colloidal polymer particles of high molar mass. Micro-emulsion polymerization is also an effective approach for nano-sized polymeric nanoparticles. The particle size and average number of chains per particle are smaller in this polymerization [17]. Table 1 shows the differences among various emulsions techniques [18-20]. In typical emulsion polymerization, usually water soluble initiator is added to thermodynamically stable emulsion. The emulsion possess swollen micelles. These particles with monomer and initiator are completely covered with the surfactant molecules. The polymer chains are formed in the micelles. The emulsions are finally broken due to increase in the particle size of micelles.

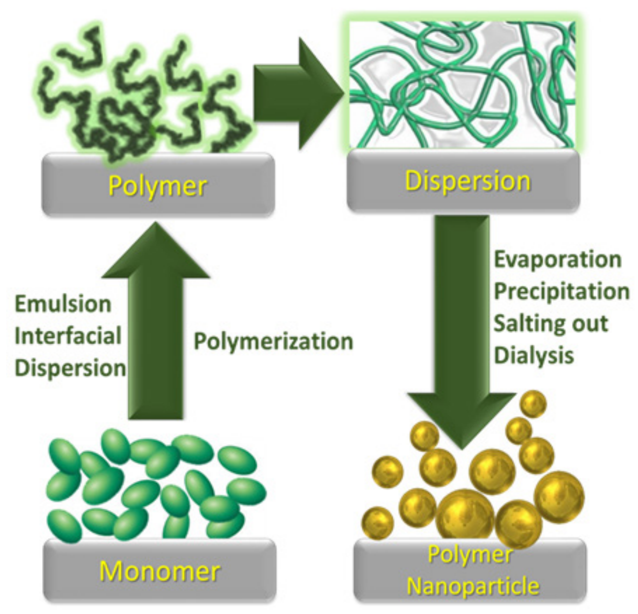

Figure 1: Preparation of polymer nanoparticles from monomers.

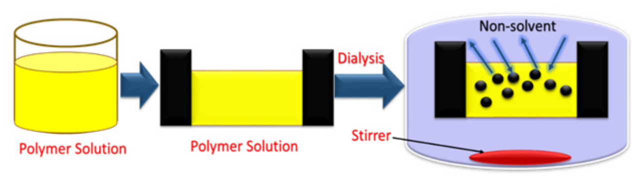

Figure 2: Schematic of osmosis method for polymer nanoparticles.

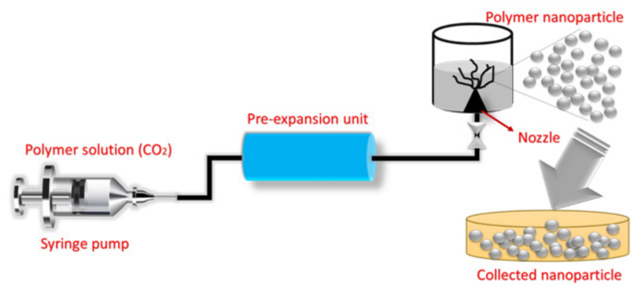

Figure 3: Schematic of rapid expansion of supercritical fluid solution.

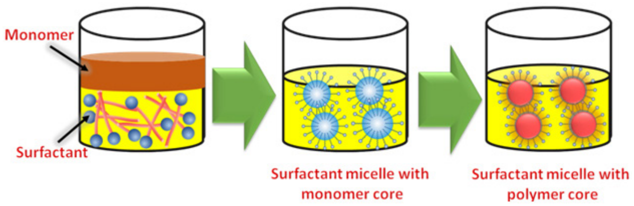

Figure 4: Representation of emulsion polymerization process.

Table 1: Comparison of emulsion polymerization systems.

	Particle size	Droplet size	Polydispersity
Emulsion	<300 nm	1-10 µm	Low
Mini-emulsion	10-30 nm	<200 nm	Very low
Micro-emulsion	<100 nm	~10 nm	Very low

Hybrid Polymeric Nanoparticles

Hybrid polymeric nanoparticles may have ability to combine the processability of polymers with mechanical, thermal, and optical properties of inorganic nanoparticles. The combination of properties may be useful for wide range of commercial, engineering, and device applications. In this regard, ordered array of silica spheres and polymer nanoparticles have been designed. The polymer nanoparticles incorporated gold nanospheres have also been designed. Thus, the core-shell particles and composite particles have been reported [21-23]. The polymeric nanoparticle have also been combined with the nanocarbons such as multi-walled carbon nanotube [24-31]. Graphene and graphene oxide (GO) nanoparticles have also been combined with the polymeric nanoparticles to form hybrid nanoparticles [32, 33]. Fullerene and nanodiamond are also excellent contenders to form combinations with the polymers to form hybrid nanoparticles [34-38]. The interactions between the polymeric nanoparticles and other organic or inorganic nanoparticles must be strengthened to avoid aggregation. The physical adsorption of polymers nanoparticle on inorganic/organic nanoparticles may lead to better dispersion and affect the rheology and viscosity of the polymer used. However, physical polymer nanoparticle-other nanoparticle interactions can be easily dissolved compared with the covalently attached nanoparticles. There have been increasing scientific interest in hybrid nanoparticles owing to high electrical conductivity, thermal conductivity, strength, stiffness, optical, and other physical properties.

Technical Significance and Outlook

From the point of view of materials chemistry, fundamental and advances of polymeric nanoparticle materials are essential to understand. Manipulation of individual nanoparticles and hybrid nanoparticles can be exploited for self-assembly procedures. Linear homopolymers have been most preferably used to develop polymeric nanoparticles. The liquid crystalline polymers and block copolymers also show high aspect ratio to promote supramolecular organizations. Hybrid polymeric nanoparticles may contribute to the development of future optical and electronic devices, engineered products for automotive and aerospace, and biomedical applications [39-41]. The hybrid polymeric nanoparticles may also be useful for coatings [42-46], textiles [47], electromagnetic interference (EMI) shielding [48, 49], and sensors [50, 51]. *In situ* generated nanoparticles and nanostructure in cross-linkable resin have yielded novel systems with improved properties. Mascia et al. [52, 53] studied the generation of siloxane domains in epoxy network to form epoxy-silica hybrids. Amine-silane functional bisphenol-A resin was reinforced with siloxane precursor using tetraethoxysilane and glycidoxypropyltrimethoxysilane coupling agent. The *in situ* developed hybrids have shown enhanced mechanical properties such as modulus, strength, and ductility, at low temperature curing. The epoxy-silica hybrids can be employed for uptake of water from environment. In another attempt, molybdate anions were introduced in epoxy-silica hybrid domains using *in situ* method [54]. Incorporation of molybdate anions in epoxy-silica network has enhanced the corrosion protection capability of the coatings. Mallakpour and Behranvand [55] designed nanoparticles using biodegradable polymers. Owing to small size and large surface area, polymeric nanoparticles have been employed in application areas such as drug delivery systems, biosensors, nanoreactors, and catalysts. Polymeric nanoparticles in delivery systems must be biocompatible and biodegradable with the living systems in terms of non-toxicity and non-antigenicity. Polymeric nanoparticle-based materials with unique physical and chemical characteristics are also demanding for employment in bio-imaging and diagnostics. The main advantage of polymeric and hybrid nanoparticles is as composite additives. These nanofillers may have several advantageous properties relative to the traditional additives at low loading requirements. In this regard, efficient nanoparticle dispersion and nanoparticle-nanoparticle interfacial adhesion may allow exciting possibilities for developing films, coatings and membranes. There are several chemical and physical aspects associated with the polymer-based nanoparticles. Future directions and opportunities for the development of new hybrid materials must be focused. Understanding the structure-property relationship of polymer-based nanoparticle materials is challenging to discover new frontiers in these hybrids.

Summary

The field of polymer nanoparticles is relatively new and needs lot of attention on fundamentals as well as advance applications of these materials. The review offers not only primary information regarding the polymeric and hybrid nanoparticles, but also presents the fabrication strategies and future prospects of these intriguing polymer nanoparticles. Polymer nanoparticle is a state-of-the-art technology which demands appropriate monomer or polymer dispersion, initiator, surfactant, precipitant, and other optimum process conditions for the preparation of small size, high surface area, and smooth surface nanoparticles. The controlled parameters may definitely lead to the desired property enhancement of these nanoparticles. To further enhance the potential of polymer nanoparticles, various organic and inorganic nanoparticles have been processed with these nanoparticles. The hybrid polymeric nanoparticles can be used for range of potential applications where polymers alone are ineffective. Future research on the development of polymeric and hybrid polymeric nanoparticle should be focused on precise control over particle size and morphology for potential relevance. Advances may lead to the commercial utilization of polymeric nanoparticles for high performance applications.

Reference

1. Geckeler KE, Nishide H. 2010. Advanced nanomaterials. Wiley-VCH Publishers, Weinheim, Germany.
2. Zhang Q, Chuang KT. 2001. Adsorption of organic pollutants from effluents of a kraft pulp mill on activated carbon and polymer resin. *Adv Environ Res* 5(3): 251-258. https://doi.org/10.1016/S1093-0191(00)00059-9
3. Kausar A. 2015. Proton exchange fuel cell membranes of poly (benzimidazole-amide)/sulfonated polystyrene/titania nanoparticles-grafted-multi-walled carbon nanotubes. *J Plast Film Sheet* 31(1): 27-44. https://doi.org/10.1177/8756087914526879
4. Rao JP, Geckeler KE. 2011. Polymer nanoparticles: preparation techniques and size-control parameters. *Prog Polym Sci* 36(7): 887-913.
5. Nagavarma BV, Yadav HK, Ayaz A, Vasudha LS, Shivakumar HG. 2012. Different techniques for preparation of polymeric nanoparticles-a review. *Asian J Pharm Clin Res* 5(Suppl 3): 16-23.
6. Vauthier C, Bouchemal K. 2009. Methods for the preparation and manufacture of polymeric nanoparticles. *Pharmaceut Res* 26(5): 1025-1058. https://doi.org/10.1007/s11095-008-9800-3
7. Kausar A. 2015. Polyaniline composites with nanodiamond, carbon nanotube and silver nanoparticle: preparation and properties. *Am J Polym Sci Engineer* 39(2): 149-160.
8. Kausar A. 2016. Synthesis and electrical property of polythiophene/sol-gel silver nanoparticle-based polyethylene composite. *Int J Compos Mater* 6(2): 43-47. https://doi.org/10.5923/j.cmaterials.20160602.01
9. Saunders BR. 2012. Hybrid polymer/nanoparticle solar cells: preparation, principles and challenges. *J Colloid Interface Sci* 369(1): 1-5. https://doi.org/10.1016/j.jcis.2011.12.016
10. Lin YY, Chen CW, Chang J, Lin TY, Liu IS, et al. 2006. Exciton dissociation and migration in enhanced order conjugated polymer/nanoparticle hybrid materials. *Nanotechnology* 17(5): 1260. https://doi.org/10.1088/0957-4484/17/5/017
11. Couvreur P. 1988. Polyalkylcyanoacrylates as colloidal drug carriers. *Crit Rev Ther Drug Carr Syst* 5(1): 1-20.
12. Vauthier C, Couvreur P. 2000. Development of nanoparticles made of polysaccharides as novel drug carrier systems. In: Wise DL (ed) Handbook of Pharmaceutical Controlled Release Technology. Marcel Dekker Inc, NY, USA, pp 13-429.
13. Couvreur P, Dubernet C, Puisieux F. 1995. Controlled drug delivery with nanoparticles: current possibilities and future trends. *Eur J Pharm Biopharm* 41(1): 2-13.
14. Geckeler KE, Stirn J. 1993. Polyreactions-mechanisms, systematics, relevance. *Naturwissenschaften* 80(11): 487-500. https://doi.org/10.1007/BF01140804
15. Chronopoulou L, Fratoddi I, Palocci C, Venditti I, Russo MV. 2009. Osmosis based method drives the self-assembly of polymeric chains into micro and nanostructures. *Langmuir* 25(19): 11940-11946. https://doi.org/10.1021/la9016382
16. Sun YP, Rolling HW, Bandara J, Meziani JM, Bunker CE. 2002. Preparation and processing of nanoscale materials by supercritical fluid technology. In: Sun YP (ed) Supercritical Fluid Technology in Materials Science and Engineering: Synthesis, Properties, and Applications. Marcel Dekker, NY, pp 491-576.
17. Puig JE. 1996. Microemulsion polymerization (oil-in water). In: Salamone JC (ed) Polymeric Materials Encyclopedia, CRC Press, Boca Raton, FL, USA, pp 4333-4341.
18. El Aasser MS, Miller CM. 1997. Preparation of latexes using miniemulsions. In: Asua JM (ed) Polymeric Dispersions: Principles and Applications, NATO Science Series E: Applied Sciences (Vol. 335), Kluwer Academic Publishers, Dordrecht, Netherlands, pp 109-26.
19. Qiu J, Charleux B, Matyjaszewski K. 2001. Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems. *Prog Polym Sci* 26(10): 2083-2134. https://doi.org/10.1016/S0079-6700(01)00033-8
20. Candau F. 1992. Polymerizations in microemulsions. In: Paleos CM (ed) Polymerization in Organized Media, Gordon & Breach Science Publishers, Philadelphia, PA, USA, pp 215-282.
21. Salvador-Morales C, Zhang L, Langer R, Farokhzad OC. 2009. Immunocompatibility properties of lipid–polymer hybrid nanoparticles with heterogeneous surface functional groups. *Biomaterials* 30(12): 2231-2240. https://doi.org/10.1016/j.biomaterials.2009.01.005
22. Mandal B, Bhattacharjee H, Mittal N, Sah H, Balabathula P, et al. 2013. Core–shell-type lipid–polymer hybrid nanoparticles as a drug delivery platform. *Nanomed Nanotechnol Biol Med* 9(4): 474-491. https://doi.org/10.1016/j.nano.2012.11.010
23. Bertrand N, Wu J, Xu X, Kamaly N, Farokhzad OC. 2014. Cancer nanotechnology: the impact of passive and active targeting in the era of modern cancer biology. *Adv Drug Deliv Rev* 66: 2-5. https://doi.org/10.1016/j.addr.2013.11.009
24. Ma PC, Tang BZ, Kim JK. 2008. Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites. *Carbon* 46(11): 1497-1505. https://doi.org/10.1016/j.carbon.2008.06.048
25. Zhang M, Su L, Mao L. 2006. Surfactant functionalization of carbon nanotubes (CNTs) for layer-by-layer assembling of CNT multi-layer films and fabrication of gold nanoparticle/CNT nanohybrid. *Carbon* 44(2): 276-283.
26. Rangari VK, Mohammad GM, Jeelani S, Hundley A, Vig K, et al. 2010. Synthesis of Ag/CNT hybrid nanoparticles and fabrication of their nylon-6 polymer nanocomposite fibers for antimicrobial applications. *Nanotechnology* 21(9): 095102. https://doi.org/10.1088/0957-4484/21/9/095102
27. Kausar A. 2014. Mechanical, thermal, and electrical properties of epoxy matrix composites reinforced with polyamide-grafted-MWCNT/poly (azo-pyridine-benzophenone-imide)/polyaniline nanofibers. *Int J Polym Mater Polym Biomater* 63(16): 831-839. https://doi.org/10.1080/00914037.2014.886220
28. Kausar A, Ashraf R. 2014. 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* 30(4): 369-387. https://doi.org/10.1177/8756087913518546
29. Kausar A, Hussain ST. 2014. Poly (azo-ether-imide) nanocomposite films reinforced with nanofibers electrospun from multi-walled carbon nanotube filled poly (azo-ether-imide). *J Plast Film Sheet* 30(3): 266-283. https://doi.org/10.1177/8756087913498884
30. Kausar A. 2014. Synthesis and properties of melt processed poly (thiourea-azosulfone)/carbon nanotubes nanocomposites. *Chinese J Polym Sci* 32(1): 64-72. https://doi.org/10.1007/s10118-014-1379-z
31. Kausar A. 2014. Novel water purification membranes of polystyrene/multi-walled carbon nanotube-grafted-graphene oxide hybrids. *Am J Polym Sci* 4: 63-72. https://doi.org/10.1007/s10118-014-1379-z
32. Kausar A. 2016. Bucky papers of poly(methyl methacrylate-co-methacrylic acid)/polyamide 6 and graphene oxide-montmorillonite. *J Dispers Sci Technol* 37(1): 66-72. https://doi.org/10.1080/01932691.2015.1027908

33. Kausar A, Rahman AU. 2016. Effect of graphene nanoplatelet addition on properties of thermo-responsive shape memory polyurethane-based nanocomposite. *Fuller Nanotub Carb Nanostruct* 24(4): 235-242. https://doi.org/10.1080/1536383X.2016.1144592
34. Kausar A. 2016. Estimation of thermo-mechanical and fire resistance profile of epoxy coated polyurethane/fullerene composite films. *Fuller Nanotub Carb Nanostruct* 24(6): 391-399. https://doi.org/10.1080/1536383X.2016.1172067
35. Kausar A, Hussain ST. 2014. Effect of modified filler surfaces and filler-tethered polymer chains on morphology and physical properties of poly (azo-pyridyl-urethane)/multi-walled carbon nanotube nanocomposites. *J Plast Film Sheet* 30(2): 181-204. https://doi.org/10.1177/8756087913493633
36. Kausar A. 2016. Nanodiamond tethered epoxy/polyurethane interpenetrating network nanocomposite: physical properties and thermoresponsive shape-memory behavior. *Int J Polym Anal Characterizat* 21(4): 348-358. https://doi.org/10.1080/1023666X.2016.1156911
37. Kausar A. 2016. Waterborne polyurethane-coated polyamide/fullerene composite films: mechanical, thermal, and flammability properties. *Int J Polym Anal Characterizat* 21(4): 275-285. https://doi.org/10.1080/1023666X.2016.1147729
38. Kausar A. 2016. Enhanced electrical and thermal conductivity of modified poly (acrylonitrile-co-butadiene)-based nanofluid containing functional carbon black-graphene oxide. *Fuller Nanotub Carb Nanostruct* 24(4): 278-285. https://doi.org/10.1080/1536383X.2016.1153467
39. Le L, Bokare A, Erogbogbo F. 2018. Hand powered, cost effective, 3D printed nanoparticle synthesizer: effects of polymer end caps, drugs, and solvents on lipid polymer hybrid nanoparticles. *Mater Res Exp* 6: 025403. https://doi.org/10.1088/2053-1591/aaed72
40. Liu J, Cheng H, Han L, Qiang Z, Zhang X, et al. 2018. Synergistic combination therapy of lung cancer using paclitaxel-and triptolide-coloaded lipid-polymer hybrid nanoparticles. *Drug Des Devel Ther* 12: 3199-3209. https://doi.org/10.2147/DDDT.S172199
41. Sokolowski M, Bartsch C, Spiering VJ, Prévost S, Appavou MS, et al. 2018. Preparation of polymer brush grafted anionic or cationic silica nanoparticles: systematic variation of the polymer shell. *Macromolecules* 51(17): 6936-6948. https://doi.org/10.1021/acs.macromol.8b01019
42. Caruso RA, Susha A, Caruso F. 2001. Multilayered titania, silica, and laponite nanoparticle coatings on polystyrene colloidal templates and resulting inorganic hollow spheres. *Chem Mater* 13(2): 400-409. https://doi.org/10.1021/cm001175a
43. Win KY, Feng SS. 2005. Effects of particle size and surface coating on cellular uptake of polymeric nanoparticles for oral delivery of anticancer drugs. *Biomaterials* 26(15): 2713-2722. https://doi.org/10.1016/j.biomaterials.2004.07.050
44. Kausar A. 2015. 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* 1(1): 60-68.
45. Lou XW, Archer LA, Yang Z. 2008. Hollow micro-/nanostructures: synthesis and applications. *Adv Mater* 20(21): 3987-4019. https://doi.org/10.1002/adma.200800854
46. Ghosh Chaudhuri R, Paria S. 2011. Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications. *Chem Rev* 112(4): 2373-2433. https://doi.org/10.1021/cr100449n
47. Perelshtein I, Applerot G, Perkas N, Guibert G, Mikhailov S, et al. 2008. Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity. *Nanotechnology* 19(24): 245705. https://doi.org/10.1088/0957-4484/19/24/245705
48. Gass J, Poddar P, Almand J, Srinath S, Srikanth H. 2006. Superparamagnetic polymer nanocomposites with uniform Fe_3O_4 nanoparticle dispersions. *Adv Funct Mater* 16(1): 71-75. https://doi.org/10.1002/adfm.200500335
49. Wilson JL, Poddar P, Frey NA, Srikanth H, Mohomed K, et al. 2004. Synthesis and magnetic properties of polymer nanocomposites with embedded iron nanoparticles. *J Appl Phys* 95(3): 1439-1443. https://doi.org/10.1063/1.1637705
50. Nath N, Chilkoti A. 2002. A colorimetric gold nanoparticle sensor to interrogate biomolecular interactions in real time on a surface. *Anal Chem* 74(3): 504-509. https://doi.org/10.1021/ac015657x
51. Tian Z, Yu J, Wu C, Szymanski C, McNeill J. 2010. Amplified energy transfer in conjugated polymer nanoparticle tags and sensors. Nanoscale 2(10): 1999-2011. https://doi.org/10.1039/C0NR00322K
52. Lionetto F, Mascia L, Frigione M. 2013. Evolution of transient-states and properties of an epoxy-silica hybrid cured at ambient temperature. *Eur Polym J* 49(6): 1298-1313. https://doi.org/10.1016/j.eurpolymj.2013.02.001
53. Mascia L. 2005. *In situ* generated fillers: qrganic-inorganic hybrids. In: Xanthos M (ed) Functional Fillers for Plastics, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp 401-419.
54. Mascia L, Prezzi L, Wilcox GD, Lavorgna M. 2006. Molybdate-doping of networks in epoxy-silica hybrids: domain structuring and corrosion inhibition. *Prog Org Coat* 56(1): 13-22. https://doi.org/10.1016/j.porgcoat.2006.01.013
55. Mallakpour S, Behranvand V. 2016. Polymeric nanoparticles: recent development in synthesis and application. *Exp Polym Lett* 10(11): 895-913. https://doi.org/10.3144/expresspolymlett.2016.84