We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 7

Multifunctional Polymer Nanocomposites Based on Thermoplastic Polyesters

Sandra Paszkiewicz

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/66121

Abstract

Polymer nanocomposites containing carbon nanoparticles have exhibited remarkable thermal, mechanical and electrical properties. This review is concerned with a narrow sector of polymer nanocomposites, namely those based on engineering polyesters, which are of great industrial interest. The various functionalization methods of modifying carbon nanotubes and graphene derivative forms to allow interacting with polymer matrices will be summarized. Moreover, the review on the processing techniques of obtaining polymer nanocomposites with the emphasis of their effect on the final properties of the obtained material will be highlighted. The light will be also shed on the nanofiller dispersion in the polymer matrix. Finally, the opportunities and challenges in the high-performance polymer nanocomposites will be presented.

Keywords: polymer nanocomposites, thermoplastic polyesters, carbon nanoparticles

1. Introduction

Engineering polyesters, such as poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT), constitute a group of engineering thermoplastics. However, this group is now expanded by new members of the polyester family, that is, poly (trimethylene terephthalate) (PTT) and poly (ethylene-2, 6-naphthalate) (PEN). They combine excellent mechanical, electrical and thermal properties with very good chemical resistance and dimensional stability. Moreover, with excellent processing characteristics and high strength and rigidity, they are widely used in industrial applications. However, still at a commercial level the aforesaid properties, one can further improve through an addition of suitable modifying agents such as nanofillers. There is a wide array of organic and inorganic nanofillers

INTECH
open science | open minds

© 2016 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

some of which have been studied more thoroughly than others. An addition of carbon nanofillers (CNF) such as carbon nanotubes (CNT) and graphene derivative forms (GDF) may seem particularly interesting from the point of view of their influence on the enhancement of a wide array of material characteristics.

The properties of polymer nanocomposites that can be improved due to the presence of carbon nanoparticles (CNP), such as carbon nanotubes (single- and multi-walled carbon nanotubes) and graphene derivatives (graphene, expanded graphite, graphene oxide, etc.), include tensile strength, tensile modulus, toughness, thermal properties, electrical and thermal conductivity, optical and barrier properties. However, the aforementioned properties one can obtain only when the nanofillers are uniformly dispersed and aligned in the polymer matrix. However, since carbon nanoparticles usually tend to form aggregates/agglomerates due to the van der Waals interactions, obtaining proper dispersion is a critical issue. The functionalization of CNP is an effective way to prevent their aggregation, which helps for a better disperse within the polymer matrix. The second approach is the preparation method such as solution mixing, melt blending and in situ polymerization. Herein, the study on the functionalization of carbon nanoparticles and preparation of polymer nanocomposites will be emphasized.

There are several approaches for developing multifunctional polymer nanocomposites utilizing unique properties of carbon nanotubes and graphene derivatives. The key issue is the development of methods that improve the dispersion of carbon nanoparticles in the polymer matrix since the proper dispersion enhanced the properties in the strongest manner. Additionally, the light will be shed on the influence of CNP on the crystallization behavior of the selected engineering polyesters, especially on PET and PTT. Despite various methods of obtaining polymer nanocomposites, such as melt blending or in situ polymerization, there are still challenges and opportunities that need to be found in order to improve the dispersion and thus modify the interfacial interactions. Therefore, the greatest emphasis will be placed on the in situ polymerization method, which in our opinion seems to have the greatest opportunity to transfer into an industrial scale.

2. Functionalization of carbon nanoparticles (CNP)

2.1. Functionalization of CNT

Because CNT usually tend to agglomerate due to van der Waals forces, one can find dispersing and aligning CNT in the polymer matrix extremely difficult. Therefore, a valid approach toward developing high-performance polymer/CNT nanocomposites is to implement individual CNT into the polymer matrix in order to achieve better alignment and dispersion, strong interfacial interactions and improvement in the load transfer across the CNT-polymer matrix interface [1]. One can find functionalization of CNT as an effective way to prevent nanotube aggregation, which allows for a better dispersion and stabilization of the CNT within a polymer matrix. There are many approaches for functionalization of CNT, and however, defect functionalization, covalent functionalization and non-covalent functionalization [2] will be the main ones described herein.

http://dx.doi.org/10.5772/66121

In the methods of defect functionalization, defects are preferentially observed at the open ends of CNT [1]. CNT are purified by oxidative methods in order to remove amorphous carbon or metal particles from the raw materials [3, 4]. The purified single-walled carbon nanotubes (SWCNT) comprise oxidized carbon atoms in the form of –COOH group [5, 6]. In these oxidizing methods, SWCNT are fractured to very short tubes with lengths of 100–300 nm [7]. The functionalized CNT are more soluble in organic solvents than raw CNT [1].

The non-covalent functionalization of nanotubes is of particular interest because without affecting the physical properties of CNT it improves solubility and processability. This type of functionalization mostly engages surfactants, bio-macromolecules or polymers' wrapping. In one of the nondestructive purification methods, nanotubes can be transferred to the aqueous phase in the presence of surfactants [8, 9], where the nanotubes are surrounded by the hydrophobic components of the corresponding micelles. The interactions become stronger when the hydrophobic part of the amphiphilic contains aromatic group. CNT can be well dispersed in water using anionic, cationic and nonionic surfactants [10–13]. The interactions between CNT and the surfactants depend on the nature of the surfactants (its alkyl chain length, headgroup size and charge). Moreover, the dispersion of CNT in both water [14, 15] and organic solvents [16] may be further improved by the physical coupling of polymers with CNT, which can be explained by the 'wrapping' mechanism [15] attributed to the specific interactions between the polymer matrix and CNT. The supramolecular complexes can be formed when the polymers wrap around CNT [17, 18], where the π-stacking interactions between the polymer and the nanotube surface are responsible for the close coupling of the structures [1]. Moreover, the non-wrapping approaches have also been used for the dispersion and solubility of CNT in different media [19, 20]. In both cases, copolymers efficiently act as stabilizers and may be tailored so as to disperse the tubes in a variety of solvents.

In the case of covalent functionalization, the translational symmetry of CNT is discomposed by changing sp2 to sp3 carbon atoms, and thus their properties, such as electronic and transport, are affected [21]. However, this type of CNT functionalization can improve both solubility and dispersion in solvents and polymers. Moreover, such improvement can be achieved by modification of surface-bound carboxylic acid groups on the nanotubes or direct reagents to the side walls of nanotubes [1]. In general, functional groups such as carboxyl or hydroxyl groups are initiated on the CNT during the oxidation process using various oxidizing agents, among others oxygen, air, concentrated sulfuric acid, nitric acid, aqueous hydrogen peroxide and mixture of acids [7, 22]. The presence of such groups on the nanotube surface allows attaching organic [23, 24] or inorganic materials, which is important from the solubilizing point of view. However, the presence of –COOH groups on the nanotube surface is more suitable than the others groups due to a variety of chemical reactions that can be conducted with this group. In order to enhance CNT' dispersion and solubilization in solvents and in polymer matrices, CNT can be either functionalized at end caps or at the sidewall [25, 26]. Functionalization with polymer molecules (polymer grafting) [27, 28] is of particular interest from processing of polymer/CNT nanocomposites' standpoint. Two main categories, that is, "grafting to" and "grafting from" approaches, have been reported for the covalent grafting of polymers to nanotubes [1]. The "grafting to" approach consists in attaching as-prepared or

commercially available polymer molecules on CNT surface via chemical reactions, such as esterification, amidation, radical coupling, etc. [1]. In this approach, the polymer has to possess suitable reactive functional groups for preparation of composites, whereas, in the "grafting from" approach, the polymer is combined with CNT surface through polymerization of monomers in the presence of reactive CNT or CNT supported initiators. The greatest advantage of this approach is that the polymer/CNT composites can be prepared with high grafting density [1].

The last method of functionalization of CNT raised herein is the "click" chemistry that is an ideal reaction for material synthesis and modification and for self-assembly of nanomaterials. It also provides an unexpected advantage of introducing azide and alkyne groups into organic and polymer molecules, the stabilization of these groups in many reaction conditions, etc. [1]. The click chemistry benefits its toleration of other functional groups, a short reaction time, high yield, high purity and regiospecificity, as well as its suitability for the use under aqueous conditions [29]. The wide range of examples of applying the click chemistry has been presented by Sahoo et al. [1]. By using this approach, CNT can be easily functionalized with desired molecules, which enhance their importance from nanoelectronics to nanobiotechnology. The breadth of attached molecules can enhance the validity of click chemistry and opens the new prospect of CNT-based nanomaterials.

2.2. Functionalization of graphene sheets

By the reason of great interest of using graphene as a reinforcing filler of polymer matrices in order to obtain multifunctional materials, a variety of methods for the graphene surface modification has been developed [30]. Among many other factors, the nature of the interfacial interactions between the filler and the matrix has a significant impact on the final properties of the composite material. At the same time, most dispersion methods allow to obtain composites where polymer matrix and the filler interact through relatively weak dispersive forces. Thus, there is a growing research interest on introducing covalent bonding between GDF and the polymer matrix, since the chemically functionalized graphene can be processed further by solvent-assisted techniques [31]. Moreover, the proper functionalization of graphene sheet staves off further agglomeration of single-layer graphene (SLG) during reduction in solvent phase and supports the maintenance of the inherent properties of graphene. Graphene oxide (GO) has been widely employed as a starting material for the synthesis of GDF. There are several methods for producing GO from natural graphite, and however, the modified Hummers method is the most fruitful nowadays [32]. The surface of GO sheet, which is highly oxygenated, can significantly alter the van der Waals interactions and lead to a range of solubility in water and organic solvents [31], while, in order to prepare graphene, the chemical, thermal or photochemical reduction in GO needs to be carried out. Nonetheless, the GO reduction without suitable stabilizers leads to precipitation of graphite particles restacking due to the rapid and irreversible aggregation of graphene sheets. Therefore, prior to the reduction process, surface modification of GO sheets is usually carried out by covalent modifications or non-covalent functionalization, followed by reduction. The covalent modification of graphene can be achieved in four different ways: nucleophilic

http://dx.doi.org/10.5772/66121

substitution, electrophilic addition, condensation and addition [31]. The first method takes place very facilely, both at room temperature and in an aqueous medium. Thus, the nucleophilic substitution is handled to be a promising method for a large-scale production of functionalized graphene. Additionally, all types of aliphatic and aromatic amines, amino acids, amine terminated biomolecules, ionic liquids, small molecular weight polymers, etc. have been successfully applied in the preparation of functionalized graphene [31]. Electrophilic substitution reaction with graphene involves the displacement of the hydrogen atom by an electrophile. An example of such reaction can be the spontaneous grafting of aryl diazonium salt to the surface of graphene [33]. In turn, a condensation reaction is a chemical reaction in which two molecules (functional groups) combine with another in order to form one single molecule with a loss of entropy. In this case, condensation occurs with isocyanate, diisocyanate and amine compounds through the formation of amides and carbamate ester linkages [31], while, in the last method, in organic addition reactions, two or more molecules combine to form a larger molecule. Many examples of the above-mentioned method provide Kuila et al [31] in the review study on the chemical functionalization of graphene.

Similarly as in the case of CNT, the non-covalent interactions primarily involve van der Waals, hydrophobic and electrostatic forces and require the physical adsorption of suitable molecules on the surface of graphene. Non-covalent functionalization is achieved by polymer wrapping, adsorption of surfactants or small aromatic molecules, etc. [32]. Furthermore, one can utilize GDF as a support to disperse and stabilize nanoparticles [30]. Particularly interesting tend to be metallic nanoparticles that can play an important role in wide number of applications such as display devices, microelectronics, photovoltaic cells, but also in medical or biological applications. The majority of the papers concerning the preparation and applications of the new class of graphene-based materials utilize precious metals like gold [34, 35], platinum [36], palladium [37] and silver [38]. However, there is also a growing interest in the use of other metals like, iron, cooper, tin and cobalt [32]. Muszynski et al. [39] presented the preparation of graphene/metal material using organic spacers, like octadecylamine, to anchor the metallic nanoparticles to the graphene surface or organic solvents such as tetrahydrofuran, methanol and ethylene glycol. Nevertheless, the in situ synthesis of the metal nanoparticles in the presence of GO has received particular interest, as it enables control over the growth of the nanoparticles on the surface of graphene through the utilization of the precursors of the metallic particles, which are then subjected to reduction by the addition of reducing agents and reducing GO at the same time. Inasmuch as the functionalization of graphene via different chemical, electrochemical and other methods has been discussed above, and since the reduction is an essential step to obtain functionalized graphene from functionalized GO, few words will be given below. The most commonly used reducing agents that can be applied in the reduction in pure GO or functionalized GO are hydrazine monohydrate, sodium borohydrydride ($NaBH_4$), p-phenylene diamine, hydroquinone and sodium hydrosulfite [40, 41]. However, these chemicals are hazardous to human health and the environment. Therefore, some alternative methods have been recently proposed [42, 43].

3. Preparation of polymer/CNP nanocomposites

To enlarge the benefits of CNP as effective reinforcement for high strength polymer nanocomposites with at the same time improved electrical, thermal and/or barrier properties, etc., the CNP should not form aggregates/agglomerates and must be well dispersed to enhance the interfacial interactions with polymer matrix. In past review paper, several processing methods available for fabricating CNP/polymer composites based on either thermoplastic or thermosetting matrices have been described [30, 44, 45]. They mainly include melt blending, in situ polymerization and solution mixing.

3.1. Melt mixing

Melt mixing is a typical and simple method, particularly useful for thermoplastic polymer nanocomposites. It is an eco-friendly, cheap and suitable method for mass production in industrial applications. The compounding is generally achieved in a single- or twin-screw extruder where the polymer and the nanoparticles mixture are heated to form a melt [46]. CNP are mechanically dispersed in a polymer matrix using a high temperature and high shear force mixer. The shear forces help to break apart the nanofiller aggregates/agglomerates or prevent their formation. Better dispersion is achieved with MWCNT than SWCNT [47]. Moreover, by changing the process conditions, that is, screw configuration, one can better control shear and mixing. Another advantage of melt mixing is the lack of necessity of using organic solvents during the process. The prepared CNP/polymer nanocomposite (usually in the form wire) one can further processed using the typical processing techniques such as injection molding, profile extrusion, blow molding, etc. However, the large number of variables referring to the process (temperature, screw-speed and shear stress) but also to the characteristics of the nanofillers (agglomerate structure, packing density, length to diameter ratio and purity) requires proper optimization of process parameters. Additionally, the polymer matrix (mainly its viscosity) can affect the quality of the dispersion. Thus, the amount of CNT introduced in melt mixing process must be lower due to high viscosities of the composites at higher loading of CNT [48]. Most of the studies reported CNT-based nanocomposites involved polymer matrices such as polyolefins, polystyrene (PS), polycarbonate (PC) but most of all polyesters [44, 45, 49]. However, no significant improvement in mechanical properties was observed in the melt blended nanocomposites. Only in case of functionalized nanotubes that interacted with polymers containing functional groups, one can observe the enhancement in the degree of dispersion along with the enhancement in selected physical properties [50]. On the other hand, in the case of GDF/polymer nanocomposites, there are a limited number of studies. Probably, low thermal stability of most chemically modified graphene derivatives and the low bulk density of graphene makes the use of melt processing difficult. Despite the fact that high shear melt mixing has been used to fabricate GDF-based nanocomposites with polylactid (PLA) [51], PET [52], etc., high shear forces can cause buckling, rolling or shortening of graphene sheets [53], thus reducing its aspect ratio.

http://dx.doi.org/10.5772/66121

3.2. Solution mixing

Solution mixing is another approach of producing polymer nanocomposites containing CNT and GDF. This is a widely used method due to the facile nature of the process consisting of the dispersion of nanoparticles in a polymer that is dissolved in a solvent before casting in a mold and evaporating the solvent. The difficulties with obtaining proper dispersion of CNP in the solvent by simple stirring are well known. Therefore, a high power ultrasonication process, which found to be more effective, is applied more and more often. The aggregates/agglomerates of CNP can be effectively crumbled utilizing the multitasking of ultrasonication. However, the crucial challenges in solution mixing are to minimize the residual solvents [54] and obtain proper dispersion of the fillers in viscous polymeric solutions [55]. Therefore, in the case of thermoplastic polyesters, which have excellent resistance to most substances, such as acids, oxidizers (ex. hydrogen peroxide), hydrocarbon fuels, oils, and lubricants, this method does not find a wider use. Despite the fact that the solution mixing generally leads to better particle dispersion than melt mixing process, slow solvent evaporation often induces particle re-aggregation, especially since the complete drying to eliminate residual solvents is needed. The aggregated graphene or GO nanoplatelets, due to the poor solubility or gravimetric precipitation by unexfoliated graphene or GO nanosheets, are a critical problem often occurring in nanocomposites obtained via solution mixing. Therefore, in the case of GO, its thermal reduction should be carefully considered because GO can easily decompose, even at low temperatures (below 150°C). This can often lead to the local structural deformations in the polymer matrix that cause a significant loss of the physical properties in the obtained polymer nanocomposites. However, the solution mixing approach is a convenient method when residual solvents can be eliminated completely and an excellent dispersion can be achieved.

3.3. In situ polymerization

In situ polymerization method is another way for preparing homogenously distributed CNT and GDF in the polymer matrix, where nanoparticles are dispersed in monomer followed by polymerization. A higher percentage of CNP may be easily dispersed in this method, and however, the viscosity generally increases, which may cause deterioration in processability of nanocomposites [55]. In comparison with melt and solvent mixing methods, in situ polymerization may amend the dispersion state and cause better compatibility between CNP and the polymer through the introduction of additional functional (active) groups on the nanoparticles surfaces but also due to the additional step of dispersing process (mechanical stirring and ultrasonication) that can be added in advance [55–58]. Besides, this method requires monomer units and a lot of reagent for the polymerization procedure, and thus, it might be less applicable in the case of naturally existing polymers [59]. Moreover, in situ polymerization should also be performed in the solution state. Therefore, the elimination of residual solvents should be addressed when one uses the solution mixing method [55].

4. Functional properties of polymer/CNP nanocomposites

4.1. Morphology and crystallization behavior

Since properties enhancement strongly correlates with nanocomposite microstructure, proper characterization of morphology is important to establish structure-property relations for these materials. Lots of research efforts have been directed toward manufacturing polymer nanocomposites containing CNP for functional and structural applications [60, 61]. However, it is worth mentioning that the nature of the dispersion problem for CNT differs from other conventional fillers, such as spherical particles and carbon fibers, due to the small diameter in nanometer scale with high aspect ratio (>1000) and thus extremely large surface area of CNT [62]. Ma et al. [62] compared the dimensions of commonly used fillers, including carbon fibers, Al_2O_3 particles, graphite nanoplatelets (GNP) and CNT and the number of particles corresponding to a uniform filler volume fraction of 0.1% in a composite of 1.0 mm^3 cube. They found that in the composite, only two pieces of Al_2O_3 particles can be found, and this number increases to 65 thousands when GNP are added and further increases to ca. 442 million pieces when CNT are introduced, all with the same filler volume fraction. Therefore, aforementioned observation clearly displays that simply due to the sheer order of magnitude a uniform dispersion of CNT in a polymer matrix is more difficult than the other fillers. However, as mentioned above the yield of CNP/polymer nanocomposite depends on the dispersion of CNP in the matrix and interfacial interactions between the CNP and the polymer. For instance, Yoo et al. [63] prepared PET nanocomposites by melt extruding mixtures of PET and benzyl isocyanate and phenyl isocyanate functionalized MWCNT. Nanocomposites with functionalized MWCNT showed better dispersion of nanotubes in the PET matrix due to enhanced interactions between PET chains and nanotubes in comparison with pristine MWCNT/PET and MWCNT-COOH/PET nanocomposites. In turn, Jin et al. [64] used the surface-modified MWCNT having acid groups (acid-MWCNT) and diamine groups (diamine-MWCNT) in order to improve the dispersion of MWCNTs in PET matrix. Due to van der Waals interactions, pristine MWCNT exhibited high degree of aggregation, whereas, the acid-MWCNT, which has been treated with sulfuric and nitric acids, showed a lower degree of entanglement due to shortened nanotube lengths. Moreover, the diamine-MWCNT was also characterized by a lower degree of aggregation as compared to pristine MWCNT which was attributed not only to the functional groups, such as carboxyl and diamine, but also to their shorter lengths. The increased interfacial interaction was also evident in PET/diamine-MWCNT nanocomposites, resulting from good wetting of the diamine-MWCNTs in the PET matrix. This was explained by the fact that the acid and diamine groups on the surface of acid-MWCNT and diamine-MWCNT, respectively, may have reacted with PET during in situ polymerization, resulting in good dispersion of acid-MWCNT and diamine-MWCNT. Additionally, Lee et al. [65] prepared via in situ polymerization PET-based nanocomposites with two types of functionalized MWCNT: methoxybenzoyl-functionalized (MeO-MWCNT) and ethoxybenzoyl-functionalized (EtO-MWCNT) nanotubes. It was found that the PET/MWCNT system has poor MWCNT dispersion in comparison with the PET/MeO-MWCNT system. However, EtO-MWCNT in PET matrix was most homogeneously dispersed, and the

interfacial boundary between EtO-MWCNT and PET matrix was practically indiscernible. In our previous study [58], nanocomposites based on poly (ethylene terephthalate) prepared by in situ polymerization with expanded graphite (EG) were compared to those with functionalized graphite sheets (GO). It was found that no big difference in the level of filler dispersion/exfoliation was observed (SEM) between GO and EG-filled composites at the same loading of 0.4 wt.%, suggesting that at low loadings the presence of functional groups on the surface of GO does not lead to significant improvement in GO exfoliation in PET matrix. However, GO seemed to be covered with polymer matrix in the stronger manner, which might suggest that some interactions between functional groups of GO and PET matrix occurred. The presence of functional groups such as carboxylic groups on the surface of GO can improve interfacial adhesion between graphene sheets and polymer matrix mainly due to the possible interaction of hydrogen bonding between the COOH groups of GO and the ester groups in polymer matrix, as it was described above for functionalized carbon nanotubes. However, in this case, same was not observed.

In the case of research on other thermoplastic polyesters, similar remarks were made. For instance, Szymczyk et al. [66] in the in situ prepared PTT/MWCNT-COOH nanocomposites observed homogenous distribution of carbon nanotubes in the PTT matrix. Individual nanotubes, some entanglements or bundles of CNT, apparently pulled out from the matrix during fracturing are observed on the surface. Moreover, most of the nanotubes showed pulling out and sliding at the surface of nanocomposite, suggesting a limitation of load transfer. Similar observations were seen for PTT-based nanocomposites with pure (non-functionalized) MWCNT [67]. Despite the fact that control over the dispersion degree of nanotubes in a polymer matrix is difficult due to strong intermolecular forces that exist between nanoparticles, and lack of functional groups on the surface of CNT, we were able to obtain well-dispersed MWCNT in the whole volume of polymer matrix. As can be seen, the high shear forces along with alternately applied ultrasounds introduced by high-speed mechanical stirring and sonication, followed by in situ polymerization, were sufficient to disperse the MWCNT in PTT matrix. However, the residual functional groups on the surface of GNS improved both the interfacial interaction with PTT chain and stabilize the dispersion of MWCNT-COOH, thus affecting electrical conductivity [68]. Several studies on the influence of the functionalization of CNT on PBT-based nanocomposites were also published by the group of prof. Z. Roslaniec [69, 70]. In both cases, it was confirmed that functionalization of nanotubes allows for the better distribution of nanotubes in the whole volume of polymer matrix. Nanotubes seem to be wrapped with PBT matrix suggesting that a strong interaction exists between the PBT matrix and functionalized MWCNT. Moreover, the presence of a modified epoxy resin seems to stabilize the MWCNT dispersion by interaction with the PBT matrix [71]. However, there is still no study on how the influence of the modification of graphene surface affects the dispersion properties in PBT matrix. However, Fabbri et al. [72] demonstrated that all prepared PBT/graphene composites showed a good dispersion of graphene into the polymer matrix. Moreover, they proved that interfacial adhesion between polymer and graphene nanoplatelets appeared thanks to the applied in situ polymerization of the ultra-low viscosity CBT oligomers. It is also worth mentioning that Kim et al. [73] compared nanocomposites reinforced with graphite platelets to those with functionalized

graphite sheets (FGS) prepared by partial pyrolysis of graphite oxide. FGS, a thermally exfoliated graphite oxide and graphite were melt blended into PEN using a small scale, twin-screw extruder. It was found that in the case of PEN/graphite nanocomposites no delamination of graphene layers was observed, since each stack was composed of ~100 single graphene layers. This was probably due to strong van der Waals binding between the closely spaced graphene layers. As compared to PEN/graphite composites, high aspect ratio FGS exhibit better dispersion state in the whole volume of PEN matrix. The statistical analysis conducted for 88 FGS particles yielded a thickness and mean diameter of 2.9 and 222 nm (~8 single graphene layer—the interlamellar spacing equals 0.34 nm), respectively, which is far much lower than in the case of PEN/graphite nanocomposites.

In the case of semicrystalline polymers, incorporation of nanofiller (depending on its type, aspect ratio, etc.) can affect degree of crystallinity, crystallite size and spherulite structure and can even cause crystallization of otherwise amorphous polymers [73, 74]. Depending on the type of the polymer, incorporation of CNT and GDF has been reported to cause an increase [57, 63, 66, 75–77], decrease [78] or no change [79] in the degree of crystallinity of a semicrystalline polymer matrix. Changes in the polymer melting and crystallization temperature have also been reported [57, 66, 69]. Yoo et al. [63] observed that the crystallinity of the PET/functionalized MWCNT nanocomposites was significantly higher than that of the pristine and acid-treated MWCNT. Nanotubes accelerated PET crystallization via change in conformation in the ethylene glycol residue from gauche to trans conformation. In turn, graphene oxide nanosheets displayed a nucleating effect on the PET crystallization due to the increase in the onset and peak crystallization temperature of nanocomposites compared to neat PET [57]. The degree of crystallinity of the nanocomposites containing of 0.3 and 0.5 wt.% of GO was higher than for the neat PET. Analysis of nanostructure parameters for PET/0.5GO composite and neat PET has shown that non-isothermally crystallized composite and neat PET have comparable values of long period. Moreover, the study on the isothermal cold crystallization of amorphous PTT and its nanocomposites [66] revealed that the presence of MWCNT-COOH affected the crystallization rate, especially at higher concentration (0.3 wt.%) of CNT. The melting and glass transition temperatures of nanocomposites obtained by non-isothermal crystallization were not significantly affected by the presence of CNT. Moreover, nanocomposites exhibited slightly higher degree of crystallinity than neat PTT. Similarly, in PBT-based nanocomposites [69], carbon nanotubes accelerated crystallization during cooling and in consequence, the crystallization peaks of the DSC curves shifted toward higher temperatures. With increasing CNT concentration (to 0.1 wt.% oxidized SWCNT), the crystallization temperature also increased, suggesting that interactions between the CNT and the matrix occurred.

4.2. Mechanical properties

The extraordinary mechanical properties, low density and large aspect ratio [44, 45] make CNT particularly attractive as candidates for the development of CNT-reinforced polymer nanocomposites. However, the in-plane elastic modulus of pristine, defect-free graphene is approximately 1.1 TPa and is the strongest material that has ever been measured on a micron length scale [80]. In both cases, processing and dispersion of CNT and GDF including GO in

the polymeric hosts constitutes the main challenge before implementation of high-performance CNP-based nanocomposites. So as mentioned before, the chemical functionalization of the nanofillers has been found to be a feasible and effective way for improving the dispersion of CNP and interfacial bonding between the CNP and the matrix. Indeed, a wide range of polymer matrixes has been used for the development of such nanocomposites. The PET-based composites containing functionalized MWCNT showed a large increase in the tensile strength and modulus [64]. The PET-based composites containing diamine-MWCNT exhibit maximum tensile strength and modulus increases by 350 and 290% at 0.5 and 2.0 wt.%, respectively, as compared to neat PET. In turn, Yoo et al. [63] observed that the addition of MWCNT-benzyl and MWCNT-phenyl at the same loading of 3 wt.% improved the tensile strength and modulus of the PET matrix. The MWCNT-phenyl nanocomposite provided the most enhanced tensile strength. The highest modulus was obtained in the PET/MWCNT-phenyl composite. Consistently, it was concluded that the incorporation of functionalized MWCNT can make a great input to the polymer reinforcement due to the enhancement of the dispersion of MWCNT in the whole volume of polymer matrix and consequent stress transfer between MWCNT and the matrix. In addition, Szymczyk et al. [66] demonstrated that along with the increasing content of MWCNT-COOH (to 0.3 wt.%) the tensile strength and Young's modulus also increased. However, further addition of MWCNT (0.4–0.5 wt.%) lowered tensile strength and Young's modulus, but their values were still comparable or higher (modulus) to neat PTT. The values of elongation at break are higher or comparable to the neat PTT. Additionally, in PBT-based nanocomposites [69], it was observed that with an increase from 0.01 to 0.1 wt.% of oxidized SWCNT, the Young's modulus, tensile strength and strain to failure increased. This was probably due to better performance of the carbon nanotubes when incorporated in the PBT. However, in the case of GDF-based nanocomposites, not so many reports were published on the improvement in thermoplastic polyester matrices. Several different types of GDF as reinforcing agent in PET and PTT matrices were described in details in Ref. [81]. It was found that the presence of the nanoparticles resulted only in a moderate (compared to the neat polymer) increase in the mechanical properties, including tensile strength.

4.3. Thermal properties (thermal stability and dimensional stability)

The exceptional thermal properties of CNT and GDF and CNP-based materials have been harnessed as fillers to improve the thermal stability and dimensional stability of polymers.

A significant number of reports have reported increased thermal stability (typically defined by the maximum mass loss rate measured by thermogravimetric methods) of polymers using CNT and GDF as nanofiller, but herein only those referring to thermoplastic polyesters will be mentioned. For instance, Yoo et al. [63] reported that the chemical modification of MWNT-COOH resulted in a higher degree of thermal degradation due to the COOH group. However, the MWCNT-benzyl and MWCNT-phenyl showed higher thermal stability than pristine MWCNT. On the other hand, Szymczyk et al. [66] showed that the thermal and oxidative stability of PTT is independent of the COOH functionalized MWCNT content. Moreover, the incorporation of expanded graphite and graphene nanoplatelets into PET and PTT matrices [81] did not affect the thermal stability of the obtained via in situ polymerization nanocom-

posites at inert atmosphere. However, the addition of CNT and GDF individually and in the mixture of both caused an enhancement of thermo-oxidative stability (shifting the beginning of the chemical decomposition temperature of up to 20–25°C).

4.4. Electrical conductivity

CNP exhibit high aspect ratio and high electrical conductivity, which makes them excellent candidates for conducting composites. Percolation theory predicts that there is a critical concentration at which composites containing conducting fillers in the insulating polymer matrices become electrically conductive. The electrical percolation threshold in polymer/CNT nanocomposites depends on the dispersion [82], alignment [82, 83], aspect ratio [82], degree of surface modification [84] of CNT, polymer types [44, 45] and composite processing methods [82]. However, in the case of GDF, although GO can be readily dispersed in many solvents (even in water) and provides functional groups that allow for better interactions with polymer chains, it is electrically insulating and thermally unstable [85]. Therefore, at least partial reduction in graphene oxide is necessary to restore electrical conductivity. Bauhofer and Kovacs [86] reviewed experimental and theoretical work on electrical percolation of carbon nanotubes (CNT) in polymer composites. They gave a comprehensive survey of published data together with an attempt of systematization. Therefore, only some newer papers on the polymer/CNT nanocomposites will be mentioned along with review on the GDF-based nanocomposites. Zhang et al. [52] presented that the electrical conductivity of PET/graphene composites increased rapidly from 2.0×10^{-13} S/m to 7.4×10^{-2} S/m with only small addition of graphene (from 0.47 to 1.2 vol.%). On the other hand, the percolation threshold of PET/graphite composites equals to 2.4 vol.%. The incorporation of EG to the PET resulted in a sharp insulator-to-conductor transition with a percolation threshold (σ_c) as low as 0.05 wt.% [87]. Additionally, the influence of the degree of crystallinity on the conductivity was studied. Amorphous films found to be exhibited higher conductivity than semicrystalline films. In turn, Hernandez et al. [88] compared how the preparation method affects the percolation threshold. Nanocomposites prepared by direct mixing showed a low electrical percolation threshold ($\phi = 0.024$ wt.% of SWCNT) and were more transparent to light than samples prepared by in situ polymerization. However the electrical percolation threshold of 0.9 wt.% has been found for PET/MWCNT, nanocomposites prepared by coagulation method [89]. It was noticed that at 1 wt.% of MWCNT loading, the conductivity level exceeded the antistatic criterion of thin films (1×10^{-8} S/cm). By the addition of MWCNT into PTT matrix, the conductivity of nanocomposites increases by 10 orders of magnitude, approaching a value of 10^{-3} S/cm for PTT/0.3 MWCNT. The percolation threshold was below 0.1 wt.% of nanotubes' concentration. In turn, the PTT/MWCNT-COOH nanocomposites [66] at concentration below 0.2 vol.% (0.4 wt.%) exhibited strong frequency dependence of the conductivity. In addition, in PTT-based nanocomposites prepared via in situ polymerization, the effect of the EG flake size on the electrical conductivity was measured [90]. It was clearly found that smaller platelets (50 μm) enabled to obtain conductive thin polymer films with a nanoplatelet content of 0.3-0.5 wt.%. At the same time, nanocomposite based on PTT with 0.5 wt.% of EG with the flake size of 500 μm proved to be nonconductive. Moreover, Li et al. [91] demonstrated that the electrical volume resistivities decreased dramatically at the exfoliated graphite (E × G)content between 3.0 and 5.0 wt.% for nanocompo-

sites based on PTT prepared via melt compounding. Additionally, the conductivity percolation for PEN/FGS nanocomposites was obtained with as little as 0.3 vol.% FGS, whereas 3 vol.% was required for graphite [77].

4.5. Gas barrier properties

There is a strong demand for improving the gas barrier properties of existing polymers used in food packaging applications, which require the near-perfect exclusion of gas molecules. The high aspect ratio of GDF insinuates their potential use for reducing gas permeability of polymer foils/films. Gas permeability through a polymer nanocomposite containing high aspect ratio impermeable flakes can be significantly lowered via both reduced crosssection for gas diffusion and a tortuous path mechanism [77]. Study of the oxygen transmission rate through nanocomposite and neat PET films has shown that the exfoliated structure of GO in PET matrix improved their oxygen barrier properties. The improvement in oxygen permeability for PET nanocomposite films at 0.3–0.5 wt.% loading of GO over the neat PET was approximately factors of 2–3.3. These improvements in oxygen barrier properties of PET are important from the application point of view in packing industry. Moreover, two series of PTT nanocomposites with EG with the flake size of 50 and 500 μm [91] demonstrated a significant enhancement in impermeability to CO_2 and O_2. The PTT/0.3EG50 μm and PTT/0.5EG50 μm nanocomposites showed over 10-fold improvement in barrier properties with respect to carbon dioxide. However, the hydrogen permeability of PEN with 4 wt.% FGS [77] was decreased by 60%, while the same amount of graphite reduced permeability only 25%. Gas barrier performance of composites reinforced with FGS was superior to that of graphite composites, and this was attributed to its higher aspect ratio.

5. Concluding remarks

There are number of approaches for developing high-performance CNP/polymer nanocomposites taking advantage of the unique properties of CNP. Thermoplastic polyesters were chosen as polymer matrices, due to their great importance in industrial applications. However, the crucial challenge is to develop the methods of nanofillers' dispersion improvement in the polymer matrix since it greatly affects the mechanical, electrical and thermal properties of nanocomposites. Despite diverse methods, such as melt mixing, solution processing and in situ polymerization along with chemical functionalization, challenging is to enhance the dispersion and modify interfacial interactions. One of the issues that need to be resolved is to obtain the optimal functionalization of CNT that can maximize interfacial adhesion between nanofillers and the polymer matrix. A proper functionalization of both CNT and GDF allows for strong interfacial interactions between CNP and polymer matrix, which may at the same time improve the dispersion of CNT in the whole volume of polymer matrix. Moreover, in the case of semicrystalline polymers (especially PET and PBT), by incorporating the nanofiller, one can affect the crystallization behavior and thus the morphology of the samples. Since the degree of crystallinity can indirectly affect mechanical and electrical properties of polymer nanocomposites, one should particularly pay attention to this factor. The enhancement in mechanical

properties of CNP/polymer nanocomposites may represent a compromise between carbon-carbon bond damage and increased CNP-polymer interaction due to CNP functionalization. Moreover, the incorporation of nanofillers like nanotubes or graphene reduces the thermal expansion of polymers by constraining the movement of a significant volume of polymer chains because of their interaction with the filler. Additionally, the electrical conductivity of a CNP/polymer nanocomposite is determined by the negative effect of carbon-carbon bond damage and the positive effect of improved CNP dispersion due to the chemical functionalization. However, in the case of oxidized graphene nanosheets, the partial reduction has to be employed in order to restore its conducting behavior. However, in each case, the choice and control over chemical modification of CNP are necessary. Moreover, composites containing fillers with large aspect ratio (like GDF) can impede and affect the diffusion path of penetrating molecules. Well-dispersed fillers create a tortuous path for gases. To achieve the best performance of CNP/polymer composites, it is important to choose the functionalization method, a suitable polymer matrix for CNT dispersion as well as polymer composite processing conditions. To conclude, the CNP functionalization and polymer matrix design for the dispersion of CNP and interfacial interactions between nanofiller and a polymer matrix are the key issues for the development of high-performance CNP composites.

Acknowledgements

This work is the result of the research project GEKON2/O5/266860/24/2016 funded by the National Centre for Research and Development, Poland.

Author details

Sandra Paszkiewicz

Address all correspondence to: sandra.paszkiewicz@zut.edu.pl

West Pomeranian University of Technology, Institute of Material Science and Engineering, Szczecin, Poland

References

[1] Sahoo NG, Rana S, Cho JW, Li L, Chan SH. Polymer nanocomposites based on functionalized carbon nanotubes. Progress in Polymer Science. 2013;35:837–867. doi:10.1016/j.progpolymsci.2010.03.002

[2] Hirsch A. Functionalization of single-walled carbon nanotubes. Angewandte Chemie International Edition. 2002;41(11):1853–1859. doi:10.1002/1521-3773

[3] Ebbesen TW, Ajayan PM, Hiura H, Tanigaki K. Purification of nanotubes. Nature. 1994;367:519. doi:10.1038/367519a0

[4] Nalwa HS, editor. Handbook of Nanostructured Materials and Nanotechnology. 5th ed. New York: Academic Press; 2000. 778 p.

[5] Hiura H, Ebbesen TW, Tanigaki K. Opening and purification of carbon nanotubes in high yield. Advanced Materials. 1995;7:275–276. doi:10.1002/adma.19950070304

[6] Kuznetsova A, Mawhinney DB, Naumenko V, Yates JT, Liu J, Smalley RE. Enhancement of adsorption inside of single-walled nanotubes: opening the entry ports. Chemical Physics Letters. 2000;321:292–296. doi:10.1016/S0009-2614(00)00341-9

[7] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, Lu A, Iverson T, Shelimov K, Huffman CB, Rodriguez-Macias F, Shon Y-S, Lee TR, Colbert DT, Smalley RE. Fullerene pipes. Science. 1998;280:1253–1256. doi:10.1126/science.280.5367.1253

[8] Bandow S, Rao AM, Williams KA, Thess A, Smalley RE, Eklund PC. Purification of single-wall carbon nanotubes by microfiltration. The Journal of Physical Chemistry B. 1997;101:8839–8842. doi:10.1021/jp972026r

[9] Duesberg GS, Burghard M, Muster J, Philipp GS. Separation of carbon nanotubes by size exclusion chromatography. Chemical Communication. 1998;3:435–436. doi: 10.1039/A707465D

[10] Paredes JI, Burghard M. Dispersions of individual single-walled carbon nanotubes of high length. Langmuir. 2004;20:5149–5152. doi:10.1021/la049831z

[11] Duesberg GS, Muster J, Krstic V, Burghard M, Roth S. Chromatographic size separation of single-wall carbon nanotubes. Applied Physics A. 1998;67:117–119. doi:10.1007/s003390050747

[12] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE, Schmidt J, Talmon Y. Individually suspended single-walled carbon nanotubes in various surfactants. Nano Letters. 2003;3:1379–1382. doi:10.1021/nl034524j

[13] Islam MF, Rojas E, Bergey DM, Johnson AT, Yodh AG. High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. Nano Letters. 2003;3:269–273. doi:10.1021/nl025924u

[14] Bandyopadhyaya R, Nativ-Roth E, Regev O, Yerushalmi-Rozen R. Stabilization of individual carbon nanotubes in aqueous solutions. Nano Letters. 2002;2:25–28. doi: 10.1021/nl010065f

[15] Pei X, Hu L, Liu W, Hao J. Synthesis of water-soluble carbon nanotubes via surface initiated redox polymerization and their tribological properties as water-based lubricant additive. European Polymer Journal. 2008;44:2458–2464. doi:10.1016/j.eurpolymj.2008.06.016

[16] Wu HX, Qiu XQ, Cao WM, Lin YH, Cai RF, Qian SX. Polymer-wrapped multiwalled carbon nanotubes synthesized via microwave-assisted *in situ* emulsion polymerization

and their optical limiting process. Carbon. 2007;45:2866–2872. doi:10.1016/j.carbon.2007.10.009

[17] Cheng F, Imin P, Maunders C, Botton G, Adronov A. Soluble, discrete supramolecular complexes of single-walled carbon nanotubes with fluorene-based conjugated polymers. Macromolecules. 2008;41:2304–2308. doi:10.1021/ma702567y

[18] Yang L, Zhang B, Liang Y, Yang B, Kong T, Zhang LM. *In situ* synthesis of amylose/single-walled carbon nanotubes supramolecular assembly. Carbohydrate Research. 2008;343:2463–2467. doi:10.1016/j.carres.2008.06.031

[19] Shvartzman-Cohen R, Nativ-Roth E, Baskaran E, Levi-Kalisman Y, Szleifer I, Yerushalmi-Rozen R. Selective dispersion of single-walled carbon nanotubes in the presence of polymers: the role of molecular and colloidal length scales. Journal of American Chemical Society. 2004;126:14850–14857. doi:10.1021/ja046377c

[20] Shvartzman-Cohen R, Kalisman YL, Navi-Roth E, Yerushalmi-Rozen R. Generic approach for dispersing single-walled carbon nanotubes: the strength of a weak interaction. Langmuir. 2004;20:6085–6088. doi:10.1021/la049344j

[21] Park H, Zhao J, Lu JP. Effects of sidewall functionalization on conducting properties of single wall carbon nanotubes. Nano Letters. 2006;6:916–919. doi:10.1021/nl052488d

[22] Zhang X, Sreekumar TV, Liu T, Kumar S. Properties and structure of nitric acid oxidized single wall carbon nanotube films. Journal of Physical Chemistry B. 2004;108:16435–16440. doi:10.1021/jp0475988

[23] Chen J, Rao AM, Lyuksyutov S, Itkis ME, Hamon MA, Hu H, Cohn RW, Eklund PC, Colbert DT, Smalley RE, Haddon RC. Dissolution of full-length single-walled carbon nanotubes. Journal of Physical Chemistry B. 2001;105:2525–2528. doi:10.1021/jp002596i

[24] Hamon MA, Chen J, Hui H, Chen Y, Itkis ME, Rao AM, Eklund PC, Haddon RC. Dissolution of single-walled carbon nanotubes. Advanced Materials. 1999;11:834–840. doi:10.1002/(SICI)1521-4095(199907)11:10<834:AID-ADMA834>3.0.CO;2-R

[25] Niyogi S, Hamon MA, Hu H, Zhao B, Bhowmik P, Sen R, Itkis ME, Haddon RC. Chemistry of single-walled carbon nanotubes. Account of Chemical Research. 2002;35:1105–1113. doi:10.1021/ar010155r

[26] Zhou O, Fleming RM, Murphy DW, Chen CH, Haddon RC, Ramirez AP, Glarum SH. Defects in carbon nanostructures. Science. 1994;263:1744–1747. doi:10.1126/science.263.5154.1744

[27] Baek JB, Lyons CB, Tan LS. Grafting of vapor-grown carbon nanofibers via *in situ* polycondensation of 3-phenoxybenzoic acid in poly(phosphoric acid). Macromolecules. 2004;37:8278–8285. doi:10.1021/ma048964o

[28] Jin Z, Sun X, Xu G, Goh SH, Ji W. Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites. Chemical Physics Letters. 2000;218:505–510. doi: 10.1016/S0009-2614(00)00091-9

[29] Kumar I, Rode CV. Efficient synthesis of fused 1,2,3-triazolo-deltalactams using huisgen [3+2] dipolar cycloaddition click-chemistry in water. Chemistry Letters. 2007;36:592–593. doi:10.1246/cl.2007.592

[30] Marques PAAP, Gonçalves G, Cruz S, Almeida N, Singh MK, Gracio J, Sousa ACM. Functionalized graphene nanocomposites. In: Hashim A, editor. Advances in Nanocomposite Technology. Sheffield Hallam University, UK. InTech Open Access Publisher 2011. p. 247–272.

[31] Kuila T, Bose S, Mishra AK, Khanra P, Kim NH, Lee JH. Chemical functionalization of graphene and its applications. Progress in Polymer Science. 2012;57:1061–1105. doi: 10.1016/j.pmatsci.2012.03.002

[32] Park S, Ruoff RS. Chemical methods for the production of graphenes. Nature Nanotechnology. 2009;4:217–224. doi:10.1038/nnano.2009.58

[33] Bekyarova E, Itkis ME, Ramesh P, Berger C, Sprinkle M, Herr WA, et al. Chemical modification of epitaxial graphene: spontaneous grafting of aryl groups. Journal of American Chemical Society. 2009;131:1336–1337. doi:10.1021/ja8057327

[34] Goncalves G, Marques P, Granadeiro CM, Nogueira HIS, Singh MK, Gracio J. Surface modification of graphene nanosheets with gold nanoparticles: the role of oxygen moieties at graphene surface on gold nucleation and growth. Chemistry of Materials. 2009;21:4796–4802. doi:10.1021/cm901052s

[35] Hong W, Bai H, Xu Y, Yao Z, Gu Z, Shi G. Preparation of gold nanoparticle/graphene composites with controlled weight contents and their application in biosensors. The Journal of Physical Chemistry C. 2010;114:1822–1826. doi:10.1021/jp9101724

[36] Si Y, Samulski ET. Exfoliated graphene separated by platinum nanoparticles. Chemistry of Materials. 2008;20:6792–6797. doi:10.1021/cm801356a

[37] Scheuermann GM, Rumi L, Steurer P, Bannwarth W, Mülhaupt R. Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the Suzuki-Miyaura coupling reaction. Journal of the American Chemical Society. 2009;10:1344–1354. doi:10.1021/ja901105a

[38] Shen J, Shi M, Li N, Yan B, Ma H, Hu Y, Ye M. Facile synthesis and application of Ag-chemically converted graphene nanocomposite. Nano Research. 2010;3:339–349. doi: 10.1007/s12274-010-1037-x

[39] Muszynski R, Seger B, Kamat PV. Decorating graphene sheets with gold nanoparticles. The Journal of Physical Chemistry C. 2008;112:5263–5266. doi:10.1021/jp800977b

[40] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon. 2007;45:1558–1565. doi:10.1016/j.carbon.2007.02.034

[41] Shin HJ, Kim KK, Benayad A, Yoon SM, Park HK, Jung IS, Jin MH, Jeong HK, Kim JM, Choi JY, Lee YH. Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. Advanced Functional Materials. 2009;19:1987–1992. doi:10.1002/adfm.200900167

[42] Fan X, Peng W, Li Y, Wang S, Zhang G, Zhang F. Deoxygenation of exfoliated graphite oxide under alkaline conditions: a green route to graphene preparation. Advanced Materials. 2008;20:4490–4493. doi:10.1002/adma.200801306

[43] Amarnath CA, Hong CE, Kim NH, Ku BC, Kuila T, Lee JH. Efficient synthesis of graphene sheets using pyrrole as a reducing agent. Carbon. 2011;49:3497–3502. doi: 10.1016/j.carbon.2011.04.048

[44] 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;44:1624–1652. doi: 10.1016/j.carbon.2006.02.038

[45] Moniruzzaman M, Winey KI. Polymer nanocomposites containing carbon nanotubes. Macromolecules. 2006;39:5194–5205. doi:10.1021/ma060733p

[46] Bhattacharya M. Polymer nanocomposites—a comparison between carbon nanotubes, graphene, and clay as nanofillers. Materials. 2016;9:262–297. doi:10.3390/ma9040262

[47] Grady BP. Carbon Nanotube-Polymer Composites Manufacture, Properties, and Applications. New York: John Wiley and Sons; 2011. p. 145.

[48] Guo Q. Polymer Morphology: Principles, Characterization, and Processing. New York: Wiley and Sons; 2016. p. 464.

[49] McClory C, Chin SJ, McNally T. Polymer/carbon nanotube composites. Australian Journal of Chemistry. 2009;62:762–785. doi:10.1071/CH09131

[50] Wu D, Sun Y, Zhang M. Kinetics study on melt compounding of carbon nanotube/polypropylene nanocomposites. Journal of Polymer Science Part B Polymer Physics. 2009;47:608–618. doi:10.1002/polb.21668

[51] Kim IH, Jeong YG. Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. Journal of Polymer Science Part B Polymer Physics. 2010;48:850–858. doi:10.1002/polb.21956

[52] Zhang HB, Zheng WG, Yan Q, Yang Y, Wang JW, Lu ZH, Ji GY, Yu ZZ. Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding. Polymer. 2010;51:1191–1196. doi:10.1016/j.polymer.2010.01.027

[53] An X, Simmons T, Shah R, Wolfe C, Lewis KM, Washington M, Nayak SK, Talapatra S, Kar S. Stable aqueous dispersions of noncovalently functionalized graphene from

graphite and their multifunctional high-performance applications. Nano Letters. 2010;10:4295–4301. doi:10.1021/nl903557p

[54] Verdejo R, Bernal MM, Romasanta LJ, Lopez J. Graphene filled polymer nanocomposites. Journal of Materials Chemistry. 2011;21:3301–3310. doi:10.1039/C0JM02708A

[55] Yoo BM, Shin HJ, Yoon HW, Park HB. Graphene and graphene oxide and their uses in barrier polymers. Journal of Applied Polymer Science. 2014;131:39628.

[56] Paszkiewicz S, Kwiatkowska M, Roslaniec Z, Szymczyk A, Jotko M, Lisiecki S. The influence of different shaped nanofillers (1D, 2D) on barrier and mechanical properties of polymer hybrid nanocomposites based on PET prepared by *in situ* polymerization. Polymer Composites. 2016;37:1949–1959. doi:10.1002/pc.23373

[57] Szymczyk A, Paszkiewicz S, Pawelec I, Lisiecki S, Jotko M, Spitalksy Z, Mosnacek J, Roslaniec Z. Oxygen barrier properties and melt crystallization behavior of poly(ethylene terephthalate)/graphene oxide nanocomposites. Journal of Nanomaterials. 2015;382610:10. doi:10.1155/2015/382610

[58] Paszkiewicz S, Nachman M, Szymczyk A, Spitalsky Z, Mosnacek J, Roslaniec Z. Influence of expanded graphite (EG) and graphene oxide (GO) on physical properties of PET based nanocomposites. Polish Journal of Chemical Technology. 2014;16:45–50. doi:10.2478/pjct-2014-0068

[59] Sadasivuni KK, Ponnamma D, Thomas S, Grohens Y. Evolution from graphite to graphene elastomer composites. Progress in Polymer Science. 2014;39:749–780. doi:10.1016/j.progpolymsci.2013.08.003

[60] Thostenson ET, Ren ZF, Chou TW. Advances in the science and technology of CNTs and their composites: a review. Composites Science and Technology. 2001;61:1899–1912. doi:10.1016/S0266-3538(01)00094-X

[61] Ajayan PM, Schadler LS, Braun PV. Nanocomposite Science and Technology. Weinheim: Wiley-VCH; 2003. pp. 77–80.

[62] Ma PC, 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;41:1345–1367. doi:10.1016/j.compositesa.2010.07.003

[63] Yoo HJ, Jung YC, Cho JW. Effect of interaction between poly(ethylene terephthalate) and carbon nanotubes on the morphology and properties of their nanocomposites. Journal of Polymer Science: Part B: Polymer Physics. 2008;46:900–910. doi:10.1002/polb.21424

[64] Jin SH, Park Y-B, Yoon KH. Rheological and mechanical properties of surface modified multi-walled carbon nanotube-filled PET composite. Composites Science and Technology. 2007;67:3434–3441. doi:10.1016/j.compscitech.2007.03.013

[65] Lee HJ, Oh SJ, Choi JY, Kim JW, Han J, Tan LS, Baek JB. *In situ* synthesis of poly(ethylene terephthalate) (PET) in ethylene glycol containing terephthalic acid and functionalized

multiwalled carbon nanotubes (MWNTs) as an approach to MWNT/PET nanocomposites. Chemistry of Materials. 2005;17:5057–5064. doi:10.1021/cm051218t

[66] Szymczyk A, Roslaniec Z, Zenker M, Garcia-Gutierrez M-C, Hernandez JJ, Rueada DR, Nogales A, Ezquerra TA. Preparation and characterization of nanocomposites based on COOH functionalized multi-walled carbon nanotubes and on poly(trimethylene terephthalate). Express Polymer Letters. 2011;5:977–995. doi:0.3144/expresspolymlett.2011.96

[67] Paszkiewicz S, Szymczyk A, Janowska I, Jedrzejewski R, Linares A, Ezquerra TA, Wagner TA, Roslaniec Z. Comparative study on the properties of poly(trimethylene terephthalate) based nanocomposites containing multi-walled carbon (MWCNT) and tungsten disulfide (INT-WS2) nanotubes. Polymers for Advanced Technologies. (Forthcoming).

[68] Paszkiewicz S, Szymczyk A, Kasprowiak I, Zenker M, Pilawka R, Linares A, Ezquerra TA, Roslaniec Z. Electrical and rheological characterization of poly(trimethylene terephthalate) hybrid nanocomposites filled with COOH functionalized MWCNT and graphene nanosheets. Polymer Composites. (Forthcoming).

[69] Kwiatkowska M, Broza G, Schulte K, Roslaniec Z. The *in-situ* synthesis of polybutylene terephthalate/carbon nanotubes composites. Reviews on Advanced Materials Science. 2006;12:154–159.

[70] Piesowicz E, Irska I, Bryll K, Gawdzinska K, Bratychak M. Poly(butylene terephthalate/carbon nanotubes nanocomposites. Part II. Structure and properties. Polimery. 2016;61:18–24. doi:10.14314/polimery.2016.024

[71] Fabbri P, Bassoli E, Bon SB, Valentini S. Preparation and characterization of poly (butylene terephthalate)/graphene composites by *in-situ* polymerization of cyclic butylene terephthalate. Polymer. 2010;53:897–902. doi:10.1016/j.polymer.2012.01.015

[72] Kim H, Macosko CW. Morphology and properties of polyester/exfoliated graphite nanocomposites. Macromolecules. 2008;41:3317–3327. doi:10.1021/ma702385h

[73] Schadler LS, Brinson LC, Sawyer WG. Polymer nanocomposites: a small part of the story. The Journal of the Minerals, Metals and Materials Society. 2007;59:53–60. doi:10.1007/s11837-007-0040-5

[74] Xu JZ, Chen T, Yang CL, Li ZM, Mao YM, Zeng BQ, Hsiao BS. Isothermal crystallization of poly(l-lactide) induced by graphene nanosheets and carbon nanotubes: a comparative study. Macromolecules. 2010;43:5000–5008. doi:10.1021/ma100304n

[75] Liang JJ, Huang Y, Zhang L, Wang Y, Ma YF, Guo TY, Chen Y. Molecular-level dispersion of graphene into poly (vinyl alcohol) and effective reinforcement of their nanocomposites. Advanced Functional Materials. 2009;19:2297–2302. doi:10.1002/adfm.200801776

[76] Yang X, Li L, Shang S, Tao X. Synthesis and characterization of layer-aligned poly(vinyl alcohol)/graphene composites. Polymer. 2010;51:3431–3435.

[77] Ansari S, Kelarakis A, Estevez L, Giannelis EP. Oriented arrays of graphene in a polymer matrix by *in situ* reduction of graphite oxide nanosheets. Small. 2010;6:205–209. doi: 10.1002/smll.200900765

[78] Cai D, Song M. A simple route to enhance the interface between graphite oxide nanoplatelets and asemi-crystalline polymer for stress transfer. Nanotechnology. 2009;20:315708. doi:10.1088/0957-4484/20/31/315708

[79] Du N, Zhao CY, Chen Q, Wu G, Lu R. Preparation and characterization of nylon 6/graphite composite. Material Chemistry and Physics. 2010;120:167–171. doi:10.1016/j.matchemphys.2009.10.041

[80] Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science. 2008;321:385–388. doi:0.1126/science.1157996

[81] Paszkiewicz S. Polymer hybrid nanocomposites containing carbon nanoparticles. *In situ* synthesis and physical properties. Szczecin: West Pomeranian University of Technology. 2014. p. 190. Available from: http://zbc.ksiaznica.szczecin.pl/dlibra/docmetadata?id=30212&from=publication

[82] Li J, Ma PC, Chow WS, To CK, Tang BZ, Kim JK. Correlations between percolation threshold, dispersion state, and aspect ratio of carbon. Advanced Functional Materials. 2007;17:3207–3215. doi:10.1002/adfm.200700065

[83] Choi ES, Brooks JS, Eaton DL, Al Haik MS, Hussaini MY, Garmestani H, Li D, Dahmen K. Enhancement of thermal and electrical properties of carbon nanotube polymer composites by magnetic field processing. Journal of Applied Polymer Science. 2003;94:6034. doi:10.1063/1.1616638

[84] Georgakilas V, Kordatos K, Prato M, Guldi DM, Holzingger M, Hirsch A. Organic functionalization of carbon nanotubes. Journal of the American Chemical Society. 2002;124:760–761. doi:10.1021/ja016954m

[85] Kim H, Abdala AA, Macosko CW. Graphene/polymer nanocomposites. Macromolecules. 2010;43:6515–6530. doi:10.1021/ma100572e

[86] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer nanocomposites. Composites Science and Technology. 2009;69:1486–1498. doi:10.1016/j.compscitech.2008.06.018

[87] Paszkiewicz S, Szymczyk A, Spitalsky Z, Soccio M, Mosnacek J, Ezquerra TA, Roslaniec Z. Electrical conductivity of poly(ethylene terephthalate)/expanded graphite nanocomposites prepared by *in situ* polymerization. Journal of Polymer Science Part B: Polymer Physics. 2012;50:1645–1652. doi:10.1002/polb.23176

[88] Hernandez JJ, Garcia-Gutierrez MC, Nogales A, Rueda DR, Kwiatkowska M, Szymczyk A, Roslaniec Z, Concheso A, Guinea I, Ezquerra TA. Influence of preparation procedure on the conductivity and transparency of SWCNT-polymer nanocomposites.

Composites Science and Technology. 2009;69:1867–1872. doi:10.1016/j.compscitech.2009.04.002

[89] Hu G, Zhao C, Zhang S, Yang M, Wang Z. Low percolation thresholds of electrical conductivity and rheology in poly(ethylene terephthalate) through the networks of multi-walled carbon nanotubes. Polymer. 2006;47:480–488. doi:10.1016/j.polymer.2005.11.028

[90] Paszkiewicz S, Pawelec I, Szymczyk A, Spitalsky Z, Mosnacek Z, Kochmanska A, Roslaniec Z. Effect of exfoliated graphite nanoplatelets' size on the phase structure, electrical and barrier properties of poly(trimethylene terephthalate) (PTT) based nanocomposites. Polymer Engineering and Science. 2015;55:2222–2230. doi:10.1002/pen.24107

[91] Li M, Jeong YG. Preparation and characterization of high-performance poly(trimethylene terephthalate) nanocomposites reinforced with exfoliated graphite. Macromolecular Materials and Engineering. 2011;296:159–167. doi:10.1002/mame.201000295

IntechOpen