Graphene as Reinforcing Filler

Subjects: Materials Science, Coatings & Films

Contributor: Stefano Rossi , Massimo Calovi

Graphene represents an innovative material, which possesses a unique combination of properties. The remarkable features of this material allow it to be often used as a reinforcing filler in organic based coatings. The excellent conductivity and mechanical strength properties of graphene produce a significant increase in the performance of the polymer matrix. Recently, however, scholars have focused on the barrier effect properties that can be provided by graphene flakes to obtain high corrosion resistance coatings. If well distributed in the polymeric matrix, in fact, the graphene-based sheets are able to provide a high resistance to the passage of aggressive ions, fundamental for the development of corrosion processes on the metal substrate. The distribution of graphene-based fillers, however, is a critical aspect, which can be improved by means of certain oxidation and functionalization processes of graphene flakes. Recent studies have shown the possibility of combining the excellent features of cataphoretic processes with the remarkable protective properties of graphene-based fillers in the creation of high-performance multifunctional composite coatings. The functionalized graphene oxide flakes, in the correct amount, can in fact increase the protective performance of cataphoretic coatings, as well as providing additional features such as mechanical strength and high conductivity.

graphene flakes
composite organic coatings
cataphoretic deposition
corrosion resistance performance.

1. Introduction

Graphene is a recent material of enormous academic and industrial interest, as it shows a combination of physical and mechanical properties that make it unique, suitable for specific applications that require considerable technological development.

The true discovery of graphene is attributed to Prof. Andre Geim and his former student Konstantin Novoselov: in 2004 they published a very first article on Science journal about the synthesis of graphene, obtained thanks to a mechanical exfoliation method[1].

Graphene is defined as a 2D carbon allotrope, whose atoms represent the sp^2 hybridization vertex of a hexagonal lattice, forming a honey-comb structure of monoatomic thickness with carbon-carbon bond distance equal to 0.142 nm. Each lattice is made of 3 strong σ bonds, constituted of a combination of orbitals s, p_x, and p_y, which provide high stability to the graphene structure. The p_z electron makes up the π-bonds, which form the π-band and π*-bands, responsible for most of graphene's notable electronic properties.

Thanks to its honeycomb lattice, graphene possesses unique properties, such as very high transparency of 97.7%, absorbing only 2.3% of visible light[2], and high electron mobility at room temperature, over than 2000 $cm^2/V*s$, allowing graphene to reach conductivity values of 10^6 S/m and a sheet resistance of 31 Ω/sq[3]. The intrinsic graphene thermal conductivity, dominated by diffusive and ballistic conduction at high and low temperatures, respectively[4], is about 2000-6000 W/mK[5]. This range of values is mainly due to the degree of defectiveness of the flakes[6], which can cause phonon scattering. Among the most innovative features of graphene, its remarkable properties of mechanical strength, combined with high lightness, make this material appreciated in various industrial applications. Using nanoindentation AFM, for example, it has been possible to measure the intrinsic strength of a defect-free sheet, which showed stiffness values of the order of 300-400 N/m and breaking strength equal to 42 N/m[7]. Graphene possesses also tensile strength and elastic modulus values equal to 125 GPa and 1.1 TPa[7], respectively. This material therefore shows, for the same thickness, a resistance 100 times greater compared to steel. Finally, another important property possessed by graphene is the high specific surface area, equal to 2630 m^2/g[8].

2. Graphene as An Ideal Candidate for Reinforcement in Composite Materials

These characteristics make graphene an ideal candidate for reinforcement in composite materials. In fact, it can be added in polymeric materials in the form of functionalized nanosheets, simple fillers or as intercalated films, increasing the electrical, thermal and mechanical properties of the polymeric matrix. Nowadays, graphene is used as a reinforcing filler due to its high mechanical strength[9][10], or thanks to its remarkable electrical conductivity, a feature that is often exploited to improve the conductivity of polymeric materials, in order to obtain multi-functional composites[11], suitable in electronic applications, such as in the production of electronic transistors[12]. Finally, the high thermal conductivity of graphene makes it possible to obtain polymer-based composite materials that are very promising in sensor and electronic applications, but also for structural functions[13][14].

To ensure that graphene can improve the properties of the composite coating, especially in terms of the barrier effect against the absorption of aggressive ions, the flakes must be homogeneously distributed inside the polymeric matrix. The dispersion of graphene and graphene oxide (GO) flakes is very complex: graphene sheets, in fact, tend to agglomerate, two to the van der Waals forces[15][16], while the functional groups introduced on the surface of the flakes, together with the hydrogen bonds, involve difficulties in the exfoliation of graphene oxide in polymeric matrix[17][18]. The dispersion of these types of flakes requires severe mechanical action, by means of stirring or ultrasound processes, to achieve satisfactory results[19]. Such mechanisms can offer good results exclusively with the use of graphene oxide, whose flakes possess functional groups, such as epoxy or carboxyl, which show a certain compatibility with resins that contain the same functional groups, according to the principle of similarity and intermiscibility. An alternative method to these mechanical processes is represented by the wet transfer dispersion technique. In this case, the flakes are first dispersed in water and then transferred to resin by extraction and evaporation. Also in this case, it is necessary to use graphene oxide flakes, which allow to get a stable colloidal suspension in aqueous solution. This is certainly an economical and eco-friendly process, as it does not require special organic solvents. Wet transfer method improves the dispersion stability, but is more complicated than simple mechanical dispersion, as it has to face the issue of treatment of the aqueous phase waste liquid. However, several studies report that it is possible to obtain a good distribution of graphene oxide in epoxy matrices thanks to this process[20][21].

As an alternative, graphene oxide flakes can be subject to functionalization process, a surface modification that can improve the dispersion efficiency. These methods are usually divided into covalent bonding and non-covalent physical adsorption. The chemical covalent modification processes involve the creation of covalent bonds between the functional groups present on the surface of the flakes and organic small molecules[22][23], organic polymers[24][25], and inorganic nano-oxides[26][27], according to the type of modifying groups. In literature it is possible to find several studies related to functionalization processes of graphene using organosilanes, which not only intercalate between the flakes, distancing them from each other, but also performing the task of anchoring the graphene sheets to the polymeric matrix, preventing the agglomeration[28][29]. The chemical covalent modification methods lead to the covalent bonds cleavage or ring opening reactions, introducing structural damage in the graphene flakes. In contrast, in non-covalent functionalization processes, such as electrostatic adsorption[30][31], electron orbital conjugation[32][33], or hydrogen bonding[34], the structure of graphene is kept intact, guaranteeing the remarkable properties of the nanofiller. Nowadays, covalent functionalization processes are often preferred, as different procedures can be used to modify graphene oxide flakes. These processes, however, involve defectiveness in the flakes, with a consequent decrease in the performance of graphene. For this reason, several studies of graphene oxide flakes reduction have been carried out, in an attempt to partially restore the characteristics of pure graphene. However, a complete restore of the structural damage is impossible, so the properties shown by rGO flakes cannot be as high as those possessed by graphene.

If homogeneously dispersed, graphene-based fillers can significantly improve the performance of polymer coatings. For this reason, this material is employed in various industrial fields.

For example, the ability of graphene to withstand high temperatures for a long time, maintaining good mechanical stability, makes this material perfect to improve the flame retardants properties of protective coatings, reducing the use of the typical additives materials based on halogens and phosphorous, which turned out to be toxic to humans and the environment. Graphene has been shown to possess incredible thermal stability even at an elevated temperature of ≈ 2126 °C[35]: this characteristic, together with the high thermal conductivity (2000 to 5000 $W\ m^{-1}\ K^{-1}$), heat dissipating capability, impermeability to gases and superb mechanical strength, makes graphene-based materials ideal for high temperature applications[36]. This nanofiller is therefore nowadays incorporated in polymeric coatings to improve the retardant properties such as thermal stability[37], smoke suppression[38], limiting oxygen index (LOI) value[39], melt viscosity (MFI)[40], increase in char yield[41], and anti-dripping properties[40].

Moreover, graphene can be considered a promising candidate for wear and scratch resistant coatings because it represents the thinnest[42], lightest[43] and strongest[44] known nanomaterial. This nanofiller can effectively prevent or reduce mechanical failure of polymeric coatings by strengthening and toughening the loaded surface as well as by transferring the stress throughout the structure[45].

Graphene represents also a good candidate for use as an antisticking coating agent, as superhydrophobic and superhydrophilic graphene-based coatings have been proposed to prevent particulate fouling[46]. On the other hand, the inclusion of carbon materials has already been extensively studied because of their known antibacterial, anti-settlement and salt rejection properties[47].

Finally, graphene and its derivatives have been shown to provide high barrier effect against the diffusion of corrosive species such as H_2O, O_2 and Cl^- when incorporated in organic coatings. This is one of the reasons why graphene appears as an excellent reinforcing additive to increase the corrosion resistance properties of protective polymeric layers. Over the years various studies have been carried out on the characteristics of graphene, which have confirmed that this material possesses high impermeability against molecules as discrete as helium[48]. If added in a polymeric matrix, graphene derivatives could theoretically lead to the “torturous path effect” and “nano-barrier wall effect” for the diffusing aggressive molecules. The tortuosity of this diffusion path is influenced by the fillers exfoliation and dispersion in the polymer matrix, the graphene high aspect ratio, sheets orientation, the graphene-polymer matrix interface and the crystallinity of polymer itself[49].

Over the years, various methods of deposition of organic coatings have been adopted, which are functional even in the case of composite layers containing graphene. Among these, the most used processes in the realization of polymer matrix coatings containing graphene are the dip coating[50] and spin coating[51] methods, the sol gel approach[52], the spray coating technique[53] and the electrophoretic deposition processes[54].

The latter process seems to be very promising to produce high quality graphene based coatings, as it process offers countless advantages. First of all, very high yields can be obtained (theoretically up to 100% of the resin used can be deposited), which represent a fundamental detail in a historical period in which great care is taken to avoid waste of material and to protect the environment. Furthermore, with regard to the environment, cataphoresis is considered an eco-friendly process, as it does not require the use of particular solvents.

Thanks to this deposition technique it is possible to obtain coatings with high aesthetic qualities, which possess uniform thickness (normally in the range between 5 and 40 µm) even on complex geometries of the product. The thicknesses can in fact be controlled by varying process parameters such as the duration of the electrodeposition and the voltage values applied.

In last decade several studies have been carried out relating to this deposition technique. Scientists, for example, sought to optimize process parameters, such as deposition voltage[55] or curing temperatures[56]. The effect of cataphoretic coatings on different types of substrate[57], such as aluminum alloys[58] and Zn-Mn alloys[59], has been studied, also through the application of particular pre-treatments[60]. All these studies have confirmed the excellent corrosion resistance properties of cataphoretic coatings, even in the presence of complex geometry substrates, such as metal foams[61]. Finally, ceria-titania nanoparticles were also added to cataphoretic baths to further improve the protective properties of the polymeric coatings[62].

Recently some studies have combined the excellent performance of cataphoretic deposition processes with the remarkable features of graphene-based fillers, to create multifunctional protective coatings. For example, a solution containing graphene oxide flakes was added to an epoxy-based bath, studying the possibility of making double-layer coatings, with different intrinsic properties[18]. This preliminary work has shown that it is possible to use graphene-based fillers in cataphoretic processes, optimizing the deposition parameters to obtain protective double-layer coatings.

Following this study, graphene flakes were subjected to oxidation and functionalization processes to improve their distribution within the polymer matrix of the cataphoretic bath[63]. Following oxidation in nitric acid and functionalization with trialkoxisilane, the graphene-based flakes enabled the significant improvement of the performance of a simple acrylic cataphoretic clear coat. This result was obtained mainly thanks to the functionalization process with (3-Aminopropyl)trimethoxysilane (APTMS), whose amino group showed high reactivity with the graphene oxide flakes[64], allowing a better distribution of the filler within the acrylic matrix.

The next step of this work therefore focused on optimizing the quantity of filler to be added to the cataphoretic bath. The correct amount of functionalized graphene oxide powder made it possible to obtain a real increase in the properties of the cataphoretic coatings, with excellent corrosion resistance performance, assessed both by exposure in an aggressive environment and by electrochemical characterization techniques[65]. As an example, **Figure 1** shows the presence of a single functionalized graphene oxide flake on the surface of the cataphoretic composite coating.

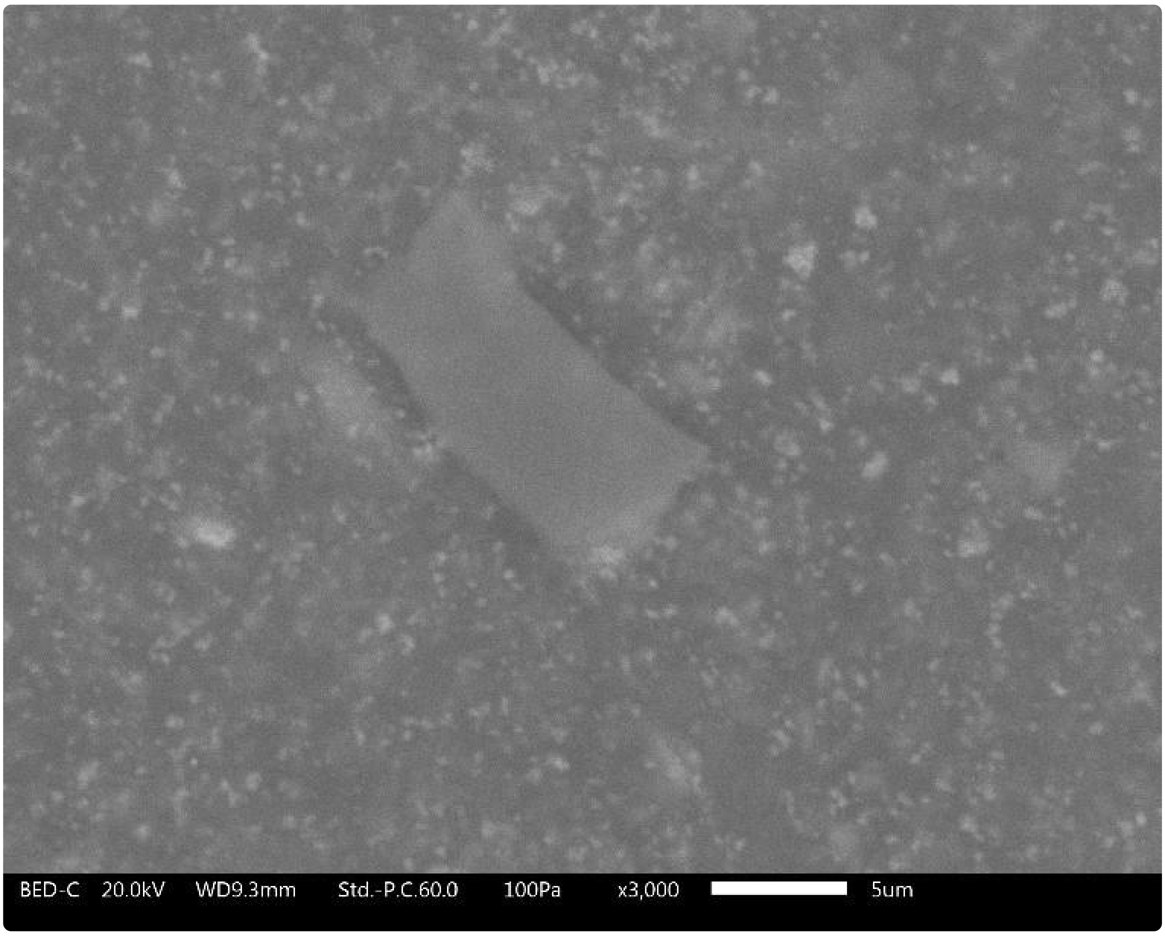

***Figure 1**: functionalized graphene oxide flake on the surface of the cataphoretic coating.*

These recent studies have shown that the cataphoretic electrodeposition process is a congenial method for the realization of protective coatings containing graphene-based fillers. The combination of the high adhesion properties of the cataphoresis with the barrier effect promoted by the graphene sheets allows to obtain layers with excellent protective features.

References

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, et al., Electric field effect in atomically thin carbon films, Science 306 (5296) (2004) 666-669.
2. R.R. Nair, P. Blake, A.N. Grigorenko, et al., Fine structure constant defines visual transparency of graphene, Science 320 (5881) (2008) 1308.
3. K.S. Kim, Y. Zhao, H. Jang, et al., Large-scale pattern growth of graphene films for stretchable transparent electrodes, Nature 457 (7230) (2009) 706-710.
4. Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and graphene oxide: synthesis, properties, and applications, Adv Mater. 22 (2010) 3906–3924.

5. S. Chen, A.L. Moore, W. Cai, J.W. Suk, J. An, C. Mishra, C. Amos, C.W. Magnuson, J. Kang, L. Shi, R.S. Ruoff, Raman measurements of thermal transport in suspended monolayer graphene of variable sizes in vacuum and gaseous environments, ACS Nano 5 (2011) 321–328
6. D.L. Nika, E.P. Pokatilov, A.S. Askerov, A.A. Balandin, Phonon thermal conduction in graphene: role of Umklapp and edge roughness scattering, Phys. Rev. B. 79 (2009).
7. C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, Science 321 (2008) 385–8.
8. M.D. Stoller, S. Park, Y. Zhu, et al., Graphene-based ultracapacitors, Nano Lett. 8 (10) (2008) 3498-3502.
9. Rafiee MA, Rafiee J, Wang Z, Song H, Yu Z-Z, Koratkar N. Enhanced mechanical properties of nanocomposites at low graphene content. ACS Nano 2009;3(12):3884–90.
10. Fang M, Wang K, Lu H, Yang Y, Nutt S. Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites. J Mater Chem 2009;19(38):7098–105.
11. Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate- treated graphene oxide nanoplatelets. Carbon 2006;44(15):3342–7.
12. Eda G, Chhowalla M. Graphene-based composite thin films for electronics. Nano Lett 2009;9(2):814–8.
13. Tang Z, Kang H, Shen Z, Guo B, Zhang L, Jia D. Grafting of polyester onto graphene for electrically and thermally conductive composites. Macromolecules 2012;45(8):3444–51.
14. Teng C-C, Ma C-CM, Lu C-H, Yang S-Y, Lee S-H, Hsiao M-C, et al. Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites. Carbon 2011;49(15):5107–16.
15. S.Y. Yang, W.N. Lin, Y.L. Huang, H.W. Tien, J.Y. Wang, C.C.M. Ma, S.M. Li, Y.S. Wang, Synergetic effects of graphene platelets and carbon nanotubes on the mechanical and thermal properties of epoxy composites, Carbon 49 (2011) 793–803. doi:10.1016/j.carbon.2010.10.014.
16. X. Wang, W. Xing, P. Zhang, L. Song, H. Yang, Y. Hu, Covalent functionalization of graphene with organosilane and its use as a reinforcement in epoxy composites, Compos. Sci. Technol. 72 (2012) 737–743. doi:10.1016/j.compscitech.2012.01.027.
17. Q. Jing, W. Liu, Y. Pan, V. V. Silberschmidt, L. Li, Z.L. Dong, Chemical functionalization of graphene oxide for improving mechanical and thermal properties of polyurethane composites, Mater. Des. 85 (2015) 808–814. doi:10.1016/j.matdes.2015.07.101.
18. S. Rossi, M. Calovi, Addition of graphene oxide plates in cataphoretic deposited organic coatings, Prog. Org. Coat. 125 (2018) 40-47. doi:10.1016/j.porgcoat.2018.08.023.

19. M. Rajabi, G.R. Rashed, D. Zaarei, Assessment of graphene oxide/epoxy nanocomposite as corrosion resistance coating on carbon steel, Corros. Eng. Sci. Technol. 50 (2014), 1743278214Y.1743278000.
20. H. Yang, C. Shan, F. Li, Q. Zhang, D. Han, L. Niu, Convenient preparation of tunably loaded chemically converted graphene oxide/epoxy resin nanocomposites from graphene oxide sheets through two-phase extraction, J. Mater. Chem. 19 (2009) 8856-8860.
21. X. Tang, Y. Zhou, M. Peng, Green preparation of epoxy/graphene oxide nanocomposites using a glycidylamine epoxy resin as the surface modifier and phase transfer agent of graphene oxide, ACS Appl. Mater. Interfaces 8 (2015) 1854-1866.
22. W. Xia, H. Xue, J. Wang, T. Wang, L. Song, H. Guo, X. Fan, H. Gong, J. He, Functionlized graphene serving as free radical scavenger and corrosion protection in gamma-irradiated epoxy composites, Carbon 101 (2016) 315-323.
23. Y. Li, Z. Yang, H. Qiu, Y. Dai, Q. Zheng, J. Li, J. Yang, Self-aligned graphene as anticorrosive barrier in waterborne polyurethane composite coatings, J. Mater. Chem. 2 (2014) 14139-14145.
24. Z. Zhang, W. Zhang, D. Li, Y. Sun, Z. Wang, C. Hou, L. Chen, Y. Cao, Y. Liu, Mechanical and anticorrosive properties of graphene/epoxy resin composites coating prepared by in-situ method, Int. J. Mol. Sci. 16 (2015) 2239-2251.
25. Y. Zhang, H.J. Chi, W.H. Zhang, Y. Sun, Q. Liang, Y. Gu, R. Jing, Highly efficient adsorption of copper ions by a PVP-reduced graphene oxide based on a new adsorptions mechanism, Nano-Micro Lett. 6 (2014) 80-87.
26. Y. Ma, H. Di, Z. Yu, L. Liang, L. Liang, P. Yang, Y. Zhang, D. Yin, Fabrication of silica-decorated graphene oxide nanohybrids and the properties of composite epoxy coatings research, Appl. Surf. Sci. 360 (2016) 936-945.
27. Z. Yu, H. Di, Y. Ma, L. Lv, Y. Pan, C. Zhang, Y. He, Fabrication of graphene oxideealumina hybrids to reinforce the anti-corrosion performance of composite epoxy coatings, Appl. Surf. Sci. 351 (2015) 986-996.
28. S. Pourhashem, M.R. Vaezi, A. Rashidi, M.R. Bagherzadeh, Distinctive roles of silane coupling agents on the corrosion inhibition performance of graphene oxide in epoxy coatings, Prog. Org. Coat. 111 (2017) 47-56.
29. S. Pourhashem, A. Rashidi, M.R. Vaezi, M.R. Bagherzadeh, Excellent corrosion protection performance of epoxy composite coatings filled with aminosilane functionalized graphene oxide, Surf. Coat. Technol. 317 (2017) 1-9.
30. Y. Fan, W. Jiang, A. Kawasaki, Highly conductive few-layer graphene/Al2O3 nanocomposites with tunable charge carrier type, Adv. Funct. Mater. 22 (2012) 3882-3889.

31. L.-B. Liu, K. Tan, J. Zhang, Preparation of polyacrylate sodium ceramic slurry dispersant and study on its dispersion mechanism, Bulletin of the Chinese Ceramic Society 24 (2005) 91-94.
32. C. Cheng, Q. Shihui, C. Mingjun, Q. Songlv, Y. Guoping, Z. Haichao, W. Liping, X. Qunji, Achieving high performance corrosion and wear resistant epoxy coatings via incorporation of noncovalent functionalized graphene, Carbon 114 (2017) 356-366.
33. T. Yang, Y. Cui, Z. Li, H. Zeng, S. Luo, W. Li, Enhancement of the corrosion resistance of epoxy coating by highly stable 3, 4, 9, 10-perylene tetracarboxylic acid functionalized graphene, J. Hazard Mater. 357 (2018) 475-482.
34. M. Ayan-Varela, J.I. Paredes, L. Guardia, S. Villar-Rodil, J.M. Munuera, M. Díaz- Gonzalez, C. Fernandez-Sanchez, A. Martínez-Alonso, J.M. Tascon, Achieving extremely concentrated aqueous dispersions of graphene flakes and catalytically efficient graphene-metal nanoparticle hybrids with flavin mononucleotide as a high-performance stabilizer, ACS Appl. Mater. Interfaces 7 (2015) 10293-10307.
35. J. Campos-Delgado, Y. A. Kim, T. Hayashi, A. Morelos- Gomez, M. Hofmann, H. Muramatsu, M. Endo, H. Terrones, R. D. Shull, M. S. Dresselhaus and M. Terrones, Thermal stability studies of CVD-grown graphene nanoribbons, Chem. Phys. Lett., 2009, 469, 177–182.
36. A. A. Balandin, Thermal properties of graphene and nanostructured carbon materials, Nat. Mater., 2011, 10, 569–581.
37. B. Yu, X. Wang, W. Xing, H. Yang, L. Song and Y. Hu, UV-Curable Functionalized Graphene Oxide/Polyurethane Acrylate Nanocomposite Coatings with Enhanced Thermal Stability and Mechanical Properties, Ind. Eng. Chem. Res., 2012, 51, 14629–14636.
38. Y. Shi, X. Qian, K. Zhou, Q. Tang, S. Jiang, B. Wang, B. Wang, B. Yu, Y. Hu and R. K. K. Yuen, CuO/Graphene Nanohybrids: Preparation and Enhancement on Thermal Stability and Smoke Suppression of Polypropylene, Ind. Eng. Chem. Res., 2013, 52, 13654–13660.
39. D. Zhuo, R. Wang, L. Wu, Y. Guo, L. Ma, Z. Weng and J. Qi, Flame Retardancy Effects of Graphene Nanoplatelet/Carbon Nanotube Hybrid Membranes on Carbon Fiber Reinforced Epoxy Composites, J. Nanomater., 2013, 2013, 7.
40. X. Wang, L. Song, H. Yang, H. Lu and Y. Hu, Synergistic Effect of Graphene on Antidripping and Fire Resistance of Intumescent Flame Retardant Poly(butylene succinate) Composites, Ind. Eng. Chem. Res., 2011, 50, 5376–5383.
41. S.-H. Liao, P.-L. Liu, M.-C. Hsiao, C.-C. Teng, C.-A. Wang, M.-D. Ger and C.-L. Chiang, One-Step Reduction and Functionalization of Graphene Oxide with Phosphorus-Based Compound to Produce Flame-Retardant Epoxy Nanocomposite, Ind. Eng. Chem. Res., 2012, 51, 4573–4581.
42. A. K. Geim and K. S. Novoselov, The rise of graphene, Nat. Mater., 2007, 6, 183– 191.

43. B. Wen, X. X. Wang, W. Q. Cao, H. L. Shi, M. M. Lu, G. Wang, H. B. Jin, W. Z. Wang, J. Yuan and M. S. Cao, Reduced graphene oxides: the thinnest and most lightweight materials with highly efficient microwave attenuation performances of the carbon world, Nanoscale, 2014, 6, 5754–5761.
44. C. Lee, X. Wei, J. W. Kysar and J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, Science, 2008, 321, 385–388.
45. L. Gong, I. A. Kinloch, R. J. Young, I. Riaz, R. Jalil and K. S. Novoselov, Interfacial stress transfer in a graphene monolayer nanocomposite, Adv. Mater., 2010, 22, 2694–2697.
46. S. Anandan, T. Narasinga Rao, M. Sathish, D. Rangappa, I. Honma and M. Miyauchi, Superhydrophilic Graphene-Loaded TiO2 Thin Film for Self-Cleaning Applications, ACS Appl. Mater. Interfaces, 2012, 5, 207–212.
47. G. Wang, L. Zhu, H. Liu and W. Li, Zinc-graphite composite coating for anti-fouling application, Mater. Lett., 2011, 65, 3095–3097.
48. M.R. Kamal, J. Uribe-Calderon, Nanoparticles and Polymer Nanocomposites, Graphite, Graphene, and Their Polymer Nanocomposites, (2013), pp. 353–392.
49. H.D. Huang, P.G. Ren, J. Chen, W.Q. Zhang, X. Ji, Z.M. Li, High barrier graphene oxide nanosheet/poly(vinyl alcohol) nanocomposite films, J. Membr. Sci. 409–410 (2012) 156–163.
50. Scriven LE. Physics and applications of dip coating and spin coating. MRS Proc. 1988; 121: 717–729.
51. Lawrence CJ, Zhou W. Spin coating of non-Newtonian fluids. J Nonnewton Fluid Mech. 1991; 39: 137–187.
52. Brinker CJ, Scherer GW. Sol-gel science: the physics and chemistry of solgel processing. Academic Press. 1990.
53. Girotto C, Rand BP, Genoe J, Heremans P. Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells. Sol Energy Mater Sol Cells. 2009; 93: 454–458.
54. Li X, Liu X, Huang J, Fan Y, Cui F. Biomedical investigation of CNT based coatings. Surf Coatings Technol. 2011; 206: 759–766.
55. S.J. García, J. Suay, Optimization of deposition voltage of cataphoretic automotive primers assessed by EIS and AC/DC/AC, Progress in Organic Coatings 66 (2009) 306–313.
56. S.J. García, M.T. Rodrıiguez, R. Izquierdo, J. Suay Evaluation of cure temperature effects in cataphoretic automotive primers by electrochemical techniques, Progress in Organic Coatings 60 (2007) 303–311.

57. C. Zanella, A. Pedrotti, M. Fedel, F. Deflorian, Influence of the electrochemical behavior of metal substrates on theproperties of cataphoretic clearcoat, Progress in Organic Coatings 77 (2014) 1987–1992.
58. V.B. Misikovic-Stankovic, M.R. Stanic, D.M. DrazЇic, Corrosion protection of aluminium by a cataphoretic epoxy coating, Progress in Organic Coatings 36 (1999) 53-63.
59. M. Bucko, V. Miskovic-Stankovic, J. Rogan, J.B. Bajat, The protective properties of epoxy coating electrodeposited on Zn–Mn alloy substrate, Progress in Organic Coatings 79 (2015) 8–16.
60. A.P. Romano, Mi. Fedel, F. Deflorian, M.G. Olivier, Silane sol–gel film as pretreatment for improvement of barrier properties and filiform corrosion resistance of 6016 aluminium alloy covered by cataphoretic coating, Progress in Organic Coatings 72 (2011) 695– 702.
61. S. Rossi, M. Calovi, M. Fedel, Corrosion protection of aluminum foams by cataphoretic deposition of organic coatings, Progress in Organic Coatings 109 (2017) 144–151.
62. L.S. Živković, B.V. Jegdić, V. Andrić, K.Y. Rhee, J.B. Bajat, V.B. Mišković-Stanković, The effect of ceria and zirconia nanoparticles on the corrosion behaviour of cataphoretic epoxy coatings on AA6060 alloy, Progress in Organic Coatings 136 (2019) 105219.
63. M. Calovi, S. Dirè, R. Ceccato, F. Deflorian, S. Rossi, Corrosion protection properties of functionalised graphene–acrylate coatings produced via cataphoretic deposition, Progress in Organic Coatings 136 (2019) 105261.
64. M. Calovi, E. Callone, R. Ceccato, F. Deflorian, S. Rossi, S. Dirè, Effect of the organic functional group on the grafting ability of trialkoxysilanes onto graphene oxide: a combined NMR, XRD and ESR study, Material 12 (2019).
65. M. Calovi, S. Rossi, F. Deflorian, S. Dirè, R. Ceccato, Effect of functionalized graphene oxide concentration on the corrosion resistance properties provided by cataphoretic acrylic coatings, Materials Chemistry and Physics 239 (2020) 121984.

Retrieved from https://encyclopedia.pub/entry/history/show/8540