

Application of Graphene in Coatings: A Survey

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Abstract

Graphene has been applied and demonstrates its excellent functions in various functional coatings by virtue of its excellent thermal, mechanical and electrical properties. This paper mainly introduces the application status and effect of graphene in conductive coating, anticorrosive coating, flame retardant coating, thermal conductive coating and high-strength coating. Finally, the application prospect of graphene in the field of coating is prospected.

Keywords: grapheme, coating; review, conductive coating, anticorrosive coating, fire retardant coating

1. Introduction

Graphene is a novel two-dimensional nano-material of sp² carbon atom, and it is a planar film whose atomic orbital hybridization is in form of sp² hybridization in hexagonal honeycomb lattice (Zhang, Z., et al, 2013.). Graphene was once thought to be a hypothetical structure. As a two-dimensional crystal, graphene could not exist independently and stably at a finite temperature (Materials N, 2007). It wasn't until 2004 that Konstantin Novoselov and Andre Geim successfully isolated graphene from graphite and demonstrated that graphene could be stable on its own. They also won the 2010 Nobel Prize in Physics for their pioneering work in the field of graphene (Meyer J C, et al. 2007. Novoselov K S, et al. 2004,2005.). Since then, graphene and its composite polymer materials have received much attention from the research community and become a hot area of research in the field of materials science. Graphene has the advantages of high electronic mobility, good thermal stability, excellent conductivity and high hardness, which has been widely used in the coatings field and has achieved excellent application results. This paper aims at summarizing the research status of graphene coatings at home and abroad, focusing on the application of graphene in the coatings field and providing guidance for the industrialization of graphene.

2. Conductive Graphene Coating

As the most conductive material in the present, graphene has a resistivity of only $10 \Omega \cdot m$, and because of its conjugate structure, it has very high electron mobility and thus has excellent electrical conductivity. Conventional conductive coatings are classified into intrinsic conductive coatings and additive conductive coatings. Intrinsic conductive coating relies on the conductivity of the resin to achieve conductivity, mainly polyaniline and polypyrrole, whose processing is difficult; the additive conductive coating achieves the conductive function by using the metal powder and the carbon powder as the conductive material. However, the metal powder as conductive material has problems that it is easy to settle and not resistance to oxidation. As a result, more preferred carbon-based powder as additive conductive coating becomes a mainstream conductive coating with better performance of the conductivity and mechanical properties. Since the graphene has a large specific surface area and low conductivity permeation threshold, the amount of unit addition required to achieve the conductive function is small. Polyaniline graphene composite (PANI/RGO) was prepared by one-step emulsion polymerization, which has excellent conductivity, good thermal stability, water-dispersibility,

antistatic property, adhesion, flexibility, impact-resistance and acid resistance (Zhao Y, 2017); (Wang Yanfeng, 2016) synthesized nano-ferrite/graphene composites and rod ferrite/graphene composites by hydrothermal and solvent-thermal methods respectively, and prepared of water-based electromagnetic shielding coatings by using those composites as fillers; The redox method was used to prepare graphene coatings, and further discussed the effect of dispersion and addition on the electrical conductivity of the system (Xu Hui et al. 2015); Mixed dispersion of graphene oxide and hydrazine hydrate which is subjected to a reduction reaction to form a graphene conductive layer was prepared in (Pham et al. 2010); Amination surface functionalization was used on graphene, and added epoxide resin to prepare an electrostatic conductive coating (Zhang Yong, 2013); Graphene oxide was used to prepare a thin film and obtained a graphene transparent conductive film by chemical reduction (Zheng et al. 2013. Nekahi et al.2014. Wang et al. 2012).

3. Anticorrosive Graphene Coating

Graphene has a large specific surface area, nanometer size, and flaky structure, which has excellent insulation performance and generates a "maze effect", that is, a curved passage in the graphene coating, which can delay the penetration of the corrosive medium in contact with the surface of the substrate, so graphene can be used to enhance the corrosion resistance of the resin coating. In order to improve the wear resistance of polyurethane, graphene was used as a lubricant and a barrier material to modify the polyurethane to improve its wear resistance and corrosion resistance (Mo et al.2015); In order to solve the defects such as micropores and microbubbles generated by high temperature curing of epoxide resin, TiO₂-GO nanohybrids were experimentally synthesized to disperse and block micropores, and improved anticorrosion performance (Yu et al.2015,2016); A conductive marine heavy-duty anti-corrosion coating was developed with graphene as a filler, which greatly improved the comprehensive anti-corrosion performance of the coating (Lan Xijian et al 2014); Graphene oxide (GO), reduced graphene oxide (RGO) and functionalized graphene were used as anti-corrosion reinforcing material for waterborne polyurethane (PU) coating (Li et al. 2016); A cathodic electrophoretic deposition method was used to coat a surface of carbon steel with a graphene oxide film in order to avoid defects such as voids in the anodization process of graphene oxide (Huang H et al. 2017); The corrosion behavior of Ni-P coatings with different concentrations of reduced graphene oxide(RGO) co-deposited was studied. The morphology, composition, crystal structure and hardness of the coatings were also analyzed. Inspired by some hydrophobic biological surfaces in nature (Tamilarasan T R, et al. 2017), Biomimetic hydrophobic graphene coatings successfully prepared on Al alloy substrates (Zheng et al. 2016); (Xue et al. 2016) successfully synthesized for aluminum alloys Corroded graphene films; Long-term corrosion protection of steels was studied to use in chloride environments such as seawater (Raghupathy et al. 2017); The effect of reduced graphene oxide (RGO) and molybdenum on the corrosion resistance of bipolar plate amorphous nickel phosphorus (Ni-P) in proton exchange membrane fuel cells was discussed in (PEMFC) (Lv et al. 2016).

4. Fire Retardant Graphene Coating

Graphene has excellent thermal stability and excellent flame retardancy. In order to solve the problem of high flammability and large amount of smoke produced by epoxide resin, (Liu et al. 2016)obtained ZHS/RGO hybrids with higher flame retardancy by in-situ hydrothermal method, which was used as a flame retardant and smoke suppressant and added with epoxide resin; In order to solve the problem of poor dispersibility of pure graphene in the polymer matrix, graphene oxide was used as flame retardant and smoke suppressing synergist, waterborne acrylic emulsion as film forming material, titanium dioxide as pigment and formulated an intumescent waterborne fire retardant coating and studied its flame retardant and smoke suppression effects using a large plate combustion method, a cone calorimeter and a smoke density test method (Li Hongfei et al. 2015); A high-density PE/brominated polystyrene/graphene nanosheet composite was prepared with good dispersibility and became a flame retardant composite with excellent performance by melt blending method (Ran et al. 2015); Graphite oxide (GO) and a hyperbranched flame retardant containing nitrogen and phosphorus was functionalized, and then the obtained functional graphene oxide (FGO) was introduced into the cross-linked polyethylene(XLPE) to enhance the flame retardancy of the matrix (Hu et al. 2014); The effects of different particle sizes and shapes of carbon additives on the flame retardancy and mechanical properties of isotactic PP were studied in (Dittrich class Group 2013); An intumescent flame retarder (IFR), carbon nanotubes (CNTs) and graphene were incorporated into the PP matrix to prepare a new PP nanocomposites (Huang et al. 2014); The surface hydrophobicity of graphene was changed by functionalizing the surface functionalized graphene oxide (FGO) grafted with pentaerythritol (PER) in water, and then introduced FGO into the intumescent flame retardant polypropylene system (Xu et al. 2016); GO-modified N-containing organic zirconium phosphate was nano-composited with PP and evaluated its flame retardancy (Nie et al 2015); A covalently grafted FGO/PP nanocomposites with better flame retardant properties was reported in (Yuan et al. 2014).

5. High Thermal Conductivity and Heat Dissipation Graphene Coating

Graphene has a thermal conductivity of up to 5300 W/ (m K). Therefore, the heat-dissipating coating prepared by graphene has high thermal conductivity and the high specific surface area of graphene can increase the heat-dissipation

area of the coating and effectively reduce the surface and internal temperature of the object. At present, Grafoid in Canada has signed a cooperation agreement with Captherm to develop graphene heat-dissipating coatings for LEDs; Graphene directly dispersed in Su-8 UV curable epoxide resin to prepare photocuring coating with high conductivity and thermally conductivity was prepared in (Sangermano et al. 2015). The process of adjusting the thermal conductivity of RGO modified epoxide resin by controlling the morphology (such as average size, thickness) and degree of reduction of RGO was studied in (Sun et al. 2016); A graphene composite heat-dissipating coating was obtained by coating a layer of graphene on the surface of the infrared emitting powder (Xue Gang et al. 2013).

6. High Strength Graphene Coating

The addition of graphene coating will form a dense network structure during the curing process of the paint film, which greatly enhances the adhesion of the paint film and the substrate, significantly improves the hardness and wear resistance of the coating, and is beneficial to solve the problem of low hardness of water polyurethane coatings, while graphene can capture free radicals in the coating and prolong the life of the coating.

7. Conclusion

The excellent properties of graphene make it show great potential and application prospects in various fields, and it has become a hot spot in scientific research at home and abroad. However, there are few reports on the application of graphene and its composite materials in the field of coatings. The research is still in its infancy, and there are still some key technical problems to be solved, such as: How to produce high quality graphene on a large scale and at low cost, and how to realize the controllability of its structure; broadening of the field of graphene application and innovation of graphene functional modification method; study on the compatibility of graphene with polymer and its action mechanism in coating system as a theoretical basis provided for the application in the field of coating; how to realize the industrial molding synthesis of graphene-polymer nanocomposites and its industrial application in the field of coatings. With the deepening of research, the above problems will be gradually solved, and graphene will play an important role in promoting the development and innovation of the coatings industry.

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References

- Dittrich, B., Wartig, K. A., Hofmann, D., Mülhaupt, R., & ScharTEL, B. (2013). Flame retardancy through carbon nanomaterials, carbon black, multiwall nanotubes, expanded graphite, multi-layer graphene and graphene in polypropylene. *Polymer Degradation & Stability*, 98(8), 1495-1505. <https://doi.org/10.1016/j.polydegradstab.2013.04.009>
- Hu, W., Jing, Z., Wang, X., et al. (2014). Effect of Functionalized Graphene Oxide with Hyper-Branched Flame Retardant on Flammability and Thermal Stability of Cross-Linked Polyethylene. *Industrial & Engineering Chemistry Research*, 53(13), 5622–5622. <https://doi.org/10.1021/ie5010306>
- Huang, H., Zhang, X., Zhang, Y., et al. (2017). Synthesis of Pt/{Reduced Graphene Oxide/ Polyoxometalates}_n Composite Films and Their Electrocatalytic Performance. *Chinese Journal of Applied Chemistry*.
- Huang, G., Wang, S., Song, P., Wu, C., Chen, S., & Wang, X. (2014). Combination effect of carbon nanotubes with graphene on intumescent flame-retardant polypropylene nanocomposites. *Composites Part A*, 59(2), 18-25. <https://doi.org/10.1016/j.compositesa.2013.12.010>
- Lan, X., Zhou, F., & Feng, W. (2014). Study on graphene conductive marine anticorrosive coating. *Shanghai Coating*, 52(12), 17-20.
- Li, J., Cui, J., Yang, J., et al. (2016). Reinforcement of graphene and its derivatives on the anticorrosive properties of waterborne polyurethane coatings. *Composites Science & Technology*, 129, 30-37. <https://doi.org/10.1016/j.compscitech.2016.04.017>
- Li, H., Wang, H., Hu, Z., et al. (2015). Study on the flame retardant and smoke inhibition effect of water-based intumescence fire retardant coatings. *Coating industry*, 45 (1), 1-8.
- Liu, X., Wu, W., Qi, Y., et al. (2016). Synthesis of a hybrid zinc hydroxystannate/reduced graphene oxide as a flame retardant and smoke suppressant of epoxy resin. *Journal of Thermal Analysis & Calorimetry*, 126(2), 1-7.
- Lv, J., Liang, T., & Wang, C. (2016). The effects of molybdenum and reduced graphene oxide on corrosion resistance of amorphous nickel-phosphorus as bipolar plates in PEMFC environment. *International Journal of Hydrogen Energy*, 41(23), 9738-9745. <https://doi.org/10.1016/j.ijhydene.2016.03.104>
- Materials, N. (2007). The rise of graphene. *Nature Material*, 6(3), 183-191. <https://doi.org/10.1038/nmat1849>

- Meyer, J. C., Geim, A. K., Katsnelson, M. I., Novoselov, K. S., Booth, T. J., & Roth, S. (2007). The structure of suspended graphene sheets. *Nature*, 446(7131), 60-63. <https://doi.org/10.1038/nature05545>
- Mo, M., Zhao, W., Chen, Z., et al. (2015). Excellent tribological and anti-corrosion performance of polyurethane composite coatings reinforced with functionalized graphene and graphene oxide nanosheets. *Rsc Advances*, 5(70), 56486-56497. <https://doi.org/10.1039/C5RA10494G>
- Nekahi, A., Marashi P. H., & Haghshenas, D. (2014). Transparent conductive thin film of ultra large reduced graphene oxide monolayers. *Applied Surface Science*, 295(295), 59-65. <https://doi.org/10.1016/j.apsusc.2014.01.004>
- Nie, L., Liu, C., Liu, L., Jiang, T., Hong, J., & Huang, J. (2015). Study of the thermal stability and flame retardant properties of graphene oxide-decorated zirconium organophosphate based on polypropylene nanocomposites. *Rsc Advances*, 5(112), 92318-92327. <https://doi.org/10.1039/C5RA13850G>
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., ... & Firsov, A. A. (2004). Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306(5696), 666-669. <https://doi.org/10.1126/science.1102896>
- Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., & Geim, A. K. (2005). Two-Dimensional Atomic Crystals. *Proc Natl Acad Sci USA*, 102(30), 10451-10453. <https://doi.org/10.1073/pnas.0502848102>
- Pham, V. H., Cuong, T. V., Hur, S. H., et al. (2010). Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating. *Carbon*, 48(7), 1945-1951. <https://doi.org/10.1016/j.carbon.2010.01.062>
- Raghupathy, Y., Kamboj, A., Rekha, M. Y, et al. (2017). Copper-graphene oxide composite coatings for corrosion protection of mild steel in 3.5% NaCl. *Thin Solid Films*, 636.
- Ran, S., Guo, Z., Han, L., et al. (2015). Effect of Friedel–Crafts reaction on the thermal stability and flammability of high-density polyethylene/brominated polystyrene/graphene nanoplatelet composites. *Polymer International*, 63(10), 1835-1841. <https://doi.org/10.1002/pi.4705>
- Sangermano, M., Calvara, L., Chiavazzo, E., Ventola, L., Asinari, P., & Mittal, V., et al. (2015). Enhancement of electrical and thermal conductivity of su-8 photocrosslinked coatings containing graphene. *Progress in Organic Coatings*, 86, 143-146. <https://doi.org/10.1016/j.porgcoat.2015.04.023>
- Sun, Y., Tang, B., Huang, W., Wang, S., Wang, Z., & Wang, X., et al. (2016). Preparation of graphene modified epoxy resin with high thermal conductivity by optimizing the morphology of filler. *Applied Thermal Engineering*, 103, 892-900. <https://doi.org/10.1016/j.applthermaleng.2016.05.005>
- Tamilarasan, T. R., Sanjith, U., Shankar, M. S., et al. (2017). EFFECT OF REDUCED GRAPHENE OXIDE (rGO) ON CORROSION AND EROSION-CORROSION BEHAVIOUR OF ELECTROLESS Ni-P COATINGS. *Wear*, 390. <https://doi.org/10.1016/j.wear.2017.09.004>
- Wang, J., Liang, M., Fang, Y., et al. (2012). Rod-coating: towards large-area fabrication of uniform reduced graphene oxide films for flexible touch screens. *Advanced Materials*, 24(21), 2874-2878. <https://doi.org/10.1002/adma.201200055>
- Wang, Y. (2016). Study on preparation and properties of nano-ferrite/graphene-based waterborne electromagnetic shielding coatings [D]. *BIT*.
- Xu, H., Chen, J., Xiong, Z., et al. (2015). Preparation of graphene composite conductive coating. *Carbon Techniques*, 34(3), 23-26.
- Xu, J., Liu, J., & Li, K. (2016). Application of functionalized graphene oxide in flame-retardant polypropylene. *Journal of Vinyl & Additive Technology*, 21(4), 278-284. <https://doi.org/10.1002/vnl.21415>
- Xue, B., Yu, M., Liu, J., et al. (2016). Corrosion protective properties of silane functionalized graphene oxide film on AA2024-T3 aluminum alloy. *Journal of the Electrochemical Society*, 163(13), C798-C806.
- Xue, G., Liang, J., Zhang, X., Yuan, Y., & Wang, S. (2013). A composite reinforced radiative coating containing graphene or oxidized graphene and a preparation method thereof. *CN, CN 102964972 A*.
- Yu, Z., Di, H., Ma, Y., et al. (2015). Preparation of graphene oxide modified by titanium dioxide to enhance the anti-corrosion performance of epoxy coatings. *Surface & Coatings Technology*, 276, 471-478. <https://doi.org/10.1016/j.surfcoat.2015.06.027>
- Yuan, B., Bao, C., Song, L., Hong, N., Liew, K. M., & Hu, Y. (2014). Preparation of functionalized graphene oxide/polypropylene nanocomposite with significantly improved thermal stability and studies on the crystallization

- behavior and mechanical properties. *Chemical Engineering Journal*, 237(5), 411-420. <https://doi.org/10.1016/j.cej.2013.10.030>
- Zhang, Y. (2013). Preparation and modification of graphene and its application in antistatic coating [D]. *ECUST*.
- Zhang, Z., Hui, F., Luo, Y., et al. (2013). Advances in the application of polysiloxane. *Organosilicon Material*, 27(3), 216-222.
- Zhang, Z., Xiao, F., Luo, Y., et al. (2013). Application and industrialization of total hydrosiloxane. *Fine and specialty chemicals*, 21(7), 25-28.
- Zhao, Y., Ma, J., Chen, K., Zhang, C. D., Yao, C., Zuo, S. X., & Kong, Y. (2017). One-Pot Preparation of Graphene-Based Polyaniline Conductive Nanocomposites for Anticorrosion Coatings. *Nano*, 12(5). <https://doi.org/10.1142/S1793292017500564>
- Zheng, Q., Ip, W. H., Lin, X., et al. (2011). Transparent conductive films consisting of ultralarge graphene sheets produced by Langmuir-Blodgett assembly. *Acs Nano*, 5(7), 6039-6051. <https://doi.org/10.1021/nn2018683>
- Zheng, Z., Liu, Y., Bai, Y., et al. (2016). Fabrication of biomimetic hydrophobic patterned graphene surface with ecofriendly anti-corrosion properties for Al alloy. *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 500, 64-71. <https://doi.org/10.1016/j.colsurfa.2016.04.008>
- Zong, X. Y. U., Lv, L., Ma, Y., et al. (2016). Covalent modification of graphene oxide by metronidazole for reinforce anti-corrosion of epoxy coatings. *Rsc Advances*, 6(22), 18217-18226. <https://doi.org/10.1039/C5RA23595B>

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