Review of Polymer Self-lubricating Coatings

Qing Feng1,2, Shuai Zou1,2, Haoming Li1,2, Mingyuan Dou1,2, and Fuchuan Huang1,2, *

1College of Mechanical Engineering, Guangxi University, Nanning, 530004, Guangxi, China.
2Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, Guangxi University, Nanning 530004, China.
*Corresponding author’s e-mail: huangfuchuan@gxu.edu.cn

Abstract: In recent years, polymer self-lubricating coatings have become a research hotspot of composite materials and tribology workers because of the characteristics of matrix polymer and solid lubricant. Based on a large amount of literature at home and abroad, the characteristics, structural design and preparation technology of polymer self-lubricating coatings are reviewed, and the research trend of polymer self-lubricating coatings is prospected.

1. Introduction
Polymer matrix composites have excellent comprehensive properties. They are gradually replacing metal materials as the most potential composite materials because of their light weight, good performance and easy processing[1]. Tribological research shows that the polymer self-lubricating coating with inorganic nano particle filler has the characteristics of matrix polymer material and solid lubricant, which has become the research hotspot of composite materials and tribology workers in recent years. Peng[2] et al. studied the tribological properties of black phosphorus (BP) nano particle reinforced polytetrafluoroethylene (PTFE) film coating. Its tribological properties mainly depend on the physical and mechanical properties of polymer matrix materials and the transfer of solid lubricants between the dual surfaces and the formation of lubrication on the dual surfaces.

2. Characteristics of polymer self-lubricating coatings
Polymer-based solid lubricant coating is widely used for sliding parts in non-lubrication (dry condition), water lubrication, vacuum, low temperature or corrosive atmosphere. Generally, it has a variety of ductility and mechanical properties. It has become a new kind of lubrication and wear-resistant coating material instead of traditional metal-based solid lubricant coatings. Polymer self-lubricating coatings have the following advantages[3].

- It has good toughness, can absorb vibration, has no noise and does not damage dual material.
- A transfer film is formed on the surface of the grinding metal to isolate the direct contact between the friction surfaces, so as to reduce the friction damping.
- It is easy to plastic deformation, adapt to the grinding surface, increase the real contact area and relieve stress concentration.
- It has good anti-corrosion performance and shock absorption function, so as to avoid corrosion wear and impact wear.
It has the advantages of strong acid and alkali resistance, low cost and easy on-site construction. It is especially suitable for chemical industry, petroleum and other industrial sectors.

However, the mechanical strength, heat resistance and heat transfer performance of polymer materials are not ideal. In the condition of severe friction, polymer materials with low heat transfer performance are prone to local temperature rise and reach the heat-resistant limit, so polymer-based solid lubricant coating is not suitable for high temperature, high speed, heavy load and other working conditions.

3. Structural design of polymer self-lubricating coatings

According to the structure, solid lubrication coating materials mainly include single-layer single component coating materials, single-layer multi-component composite structure coating materials, multi-layer structure coating materials, gradient structure coating, adaptive intelligent coating, etc[4].

Due to the single component solid lubricant coating, its lubrication temperature range is narrow, so this kind of coating can only have the effect of antifriction and wear resistance in a certain temperature range or a certain environment. With the development of machining technology, multi-component solid lubricant coating can play a unique lubrication effect in a relatively harsh lubrication environment, and get rapid development and wide application. Therefore, the following mainly introduces multi-component polymer-based solid lubricant coating, which is mainly composed of basic phase, reinforced phase and lubrication phase.

3.1. Basic phase

The basic phase is a kind of material which has stable effect on composite coating and good compatibility with matrix material and coating material. At present, common polymer based solid lubricating materials mainly include polytetrafluoroethylene (PTFE), polyimide (PI), polyether-ether-ketone (PEEK), polyphenylene sulfide (PS) and formaldehyde (POM) [5].

3.1.1. PTFE. PTFE has stable chemical properties, high and low temperature resistance, non adhesion, good self lubrication, low temperature ductility, aging resistance and high insulation properties [6][7]. Due to the extremely low surface energy of PTFE, its transfer film has poor adhesion to the friction surface, which leads to severe wear when PTFE is used as friction material. In order to improve the wear resistance of PTFE, many scholars have done fruitful research work. Rudresh et al. [8] found that the addition of GF fiber can significantly improve the tribological properties of PTFE composite. Yang Jiayi et al. [9] found that the shore hardness of the modified PTFE composite filled with pitch based carbon fiber is greater than 70HD, because the compatibility of pitch based carbon fiber and PTFE is the best. Ying et al. [10] found that in the process of friction, the addition of Cu-Sn composite particles can make the composite coating of PTFE particles precipitate a lubricating film composed of composite particles, which has the effect of reducing friction and wear.

3.1.2. PI. PI has excellent low temperature resistance[11], high radiation resistance, dilute acid resistance and creep resistance[12]. Its friction performance is excellent, second only to polytetrafluoroethylene (PTFE). When it rubs against metal under dry friction, it can transfer to the friction surface and play a role of self lubrication. The static friction coefficient is close to the dynamic friction coefficient, so it has a good ability to prevent crawling. There are two kinds of wear of PI: one is that PI is gradually worn due to adhesion, ploughing, micro cutting and so on in the friction process, resulting in the exposure of the substrate and failure. The other is that PI quickly wears to the interface layer combined with the metal substrate, and then forms a thin layer of lubricating film, which can maintain a long period of low friction wear. Due to the fact that all kinds of lubricating fillers are added to PI in the actual use, the wear process of PI composite is mostly the second case [5].

Li Zhenlian et al. [13] studied the friction and wear properties of PI filled with nano calcium carbonate and graphite. By analyzing the micro morphology and the wear morphology of the dual GCr15 bearing steel, it is found that the PI friction coefficient almost does not decrease when the nano calcium
carbonate is filled alone, but the volume wear rate increases significantly. After the graphite is filled alone, the tribological properties are improved significantly. The synergistic effect of nano calcium carbonate and graphite can enhance the bonding strength of the transfer film and the dual parts when they exist together.

Zhu Min et al. [14] studied the tribological properties of composite filled with PI by PTFE and MoS2 in dry friction environment. The results show that both of them can reduce the friction coefficient of PI, and the friction coefficient of 30% MoS2 is about 50% lower than that of pure PI. The composite with 20% PTFE and 10% MoS2 has the best anti-wear performance, and its wear rate is one order of magnitude lower than that of pure PI.

3.1.3. PEEK. PEEK is a kind of semi crystalline aromatic thermoplastic polymer material, which has a large number of benzene rings in its molecular chain. Its heat resistance is comparable to PI, with excellent self-lubricating, insulation, corrosion resistance [15] and wear resistance [16]. However, pure PEEK materials have many disadvantages, such as high brittleness, poor shear resistance and high price, which limit its application. It is often modified by adding fillers to improve its strength and wear resistance. At present, the research on PEEK modification mainly focuses on fiber reinforcement, particle filling and hybrid modification [17].

Rasheva [18] et al. prepared short carbon fiber (SCF) / polytetrafluoroethylene (PTFE) / graphite / PEEK composite by injection molding technology, and studied the effect of fiber orientation on its mechanical properties and tribological properties. It is found that when the pressure is 1 MPa and the content of SCF, PTFE and graphite is 15%, 10% and 10%, the wear rate of the composite is the lowest, the tangent direction is 0.413, and the normal direction is 0.424.

M. Zalaznik et al. [19] prepared molybdenum disulfide (MoS2) / polyetheretherketone (PEEK) based composite coating. The research shows that the addition of MoS2 particles can make PEEK and metal materials form a more uniform and better adhesive transfer film when grinding each other, thus affecting the wear behavior of the composite.

3.1.4. Others. In addition, other types of polymer based lubricating coatings have also been studied. Mao Jieyong [20] prepared PPS based multi-component composite coating by dip coating method. Cui Yexiang [21] mixed the self-healing microcapsules into epoxy resin to prepare epoxy resin based self-healing coating. Yu Chuanyong et al. [22] prepared the octaaminosesquioxane (NH2-POSS) modified polyamide imide (HM-1100A) based lubrication coating.

3.2. Lubrication phase
The lubrication phase should be able to reduce the friction coefficient between the matrix and the friction dual surface. There are many kinds of solid lubricants, such as graphite with layered crystal structure, MoS2, WS2, etc. Beckford et al. [23] prepared the graphite-polydopamine (PDA)-polytetrafluoroethylene (PTFE) composite coating by adding graphite to the PTFE matrix. Graphite is lamellar carbon, and the binding force between layers is small. Under the action of tangential force, it is easy to slide between layers. The addition of graphite can effectively reduce the friction coefficient of the composite coating. MoS2 has excellent self-lubricating properties and low friction coefficient, which can improve the hardness and creep resistance of polymer materials, and improve the wear resistance of PTFE composites. Patare et al. [24] found that the addition of MoS2 reduced the wear rate of PTFE composite.

Soft metals such as Ag, Au, Pb, Sn, In et al. are also commonly used solid lubricants. They have low shear strength and good plasticity. They are easy to cut along the metal layer and have lubricity when sliding. At the same time, they have no low temperature brittleness and will not lose lubricity at low temperature. Especially, the melting points of Ag and Au are high, the chemical stability is good in the atmospheric environment, and they can be reused, so they are suitable as lubricants in coating materials [25][26]. In addition, metal oxides (Cr2O3, MoO3, etc.), fluorides (BaF2, CaF2, etc.), and some salts (BaSO4, CaSO4, SrSO4, etc.) are also effective lubricating phases.
In addition, the lubrication phase can have other materials, such as Qu et al. [27] synthesized PTFE composite filled with Cu micro particles or SiO2 nano particles. When the nano lubricating particles are added into the polymer, it is easier to firmly combine with the polymer matrix, so that the filler shows better wear performance. In addition, nano filler, as a lubricating phase, does not cause abrasive wear, so its composite generally does not damage the dual parts.

3.3. Reinforced phase

Generally, the reinforced phase should have high hardness, good compatibility with the base phase and lubricating phase, excellent high temperature oxidation resistance, certain corrosion resistance and certain mechanical strength. Adding reinforced phase into polymer self-lubricating coating can greatly improve the hardness and bearing capacity of the coating, significantly reduce the wear during the friction process, and achieve the purpose of prolonging the friction life of the coating. The commonly used reinforced phases are mainly ceramic materials, such as nitride ceramics, oxide ceramics, carbide ceramics, etc. Corni et al. [28] prepared Al2O3 / PEEK composite coating on 316L stainless steel, and studied the effect of Al2O3 ceramic content on the coating performance. The results show that the mechanical properties of Al2O3 / PEEK composite coating are significantly improved with high or low content of alumina ceramic. And the corrosion resistance of Al2O3 / PEEK composite coating is better than PEEK coating.

4. Preparation technology of polymer self-lubricating coatings

There are many preparation processes of polymer-based solid lubricant coating. The purpose of obtaining this material by different methods is to make the solid lubricant particles evenly distributed in the polymer matrix. The commonly used preparation processes are as follows.

Ma Cui et al. [29] prepared graphene / polyimide composite coating by in-situ polymerization with aminated nano graphite as filler, and the density of the coating increased significantly. Gai Zhao et al. [30] prepared three types of fiber reinforced polyimide composites by hot pressing technology. Wu et al. [31] prepared PEEK coating on aluminum substrate by plasma spraying. Long Chunguang et al. [32] prepared polyphenylene ester / graphite / MoS2 / PEEK composite by molding. Fan Zhanguo et al. [33] prepared PTFE composite coating with polyphenylene sulfide (PPS) and polyimide (PI) as composite binder by mechanical mixing, spraying and high temperature plasticizing process.

5. Conclusion and prospect

As the polymer based solid self-lubricating coating not only has the good mechanical properties, chemical corrosion resistance, radiation resistance, significant thermal stability and wear resistance of the matrix polymer material, but also has the excellent characteristics of solid lubricants, it has been widely used in all walks of life. In general, the development trend of polymer based solid self-lubricating coating is as follows.

- Develop nano lubricating filler with excellent performance. The traditional solid lubricants, such as graphene [34] and MoS2 [35], will degrade at high temperature. Recently, a new family of two-dimensional early transition metal carbides and carbonitrides, named mxenes[36]. This kind of material has the characteristics of low shear strength, high mechanical strength and self-lubricating property[37]. The tribological properties of the material as a solid lubricant added to the polymer self-lubricating coating deserve attention.

- Study on the modification of solid lubricants. Modification of solid lubricants such as inorganic nanoparticles, graphene and molybdenum disulfide [38] to enhance their compatibility with polymer matrix is also a hot topic in the future.

- Microcapsules are added to the coating, which leads to the development of intelligent coating. Microcapsule [39] technology can make the composite show the characteristics of fluid lubrication in the friction process, it can avoid the defects of fluid lubrication at the same time, which greatly enriches the further application of polymer matrix composite in the field of tribology.
Different application places have different requirements for polymer self-lubricating coating, so it is necessary to test the performance of the material under specific experimental conditions.

Acknowledgments
Supported by the Dean Project of Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, Guangxi science and technology planning project “Development, Application and Demonstration of Resource Saving and Environment Friendly LNG New Energy Bus Lubricating Materials” (Contract number: GK AC18126008), Guangxi innovation driven development special fund project “Technology Research and Development of Super Large Series Super Fine Powder Processing System of Heavy Calcium ” (Contract number: GK AA19254010).

References
[1] Su, C. (2019) Tribological properties and numerical simulation of polymer matrix composites. D. Northeast Petroleum University, 2-3.
[2] Peng, S.G., et al. (2018) Tribological behavior of polytetrafluoroethylene coating reinforced with black phosphorus nanoparticles. J. Applied Surface ence, 441(MAY31):670-677.
[3] Qiao, H.B., Guo, Q. (2004) Research progress of polymer solid lubrication wear-resistant coating. J. Mechanical Engineering Materials, (02): 1-3 +23.
[4] Chen, J.M., Lu, X.W., Li, H.X., et al. (2014) Research progress of wide temperature range solid self-lubricating coating / coating materials. J. Journal of Tribology, 34 (5): 592-600.
[5] Qiao, H.B., Tian, X.M., Wu, Fang. (2007) Research progress of polymer self-lubricating materials. J. Materials Guide, (10): 24-26.
[6] Cui, X.M. (2009) Research progress in modification of engineering plastics polytetrafluoroethylene. J. Organic Fluorine Industry, (3): 52-58.
[7] Liao, L. (2010) Polytetrafluoroethylene processing technology, filling modification and application progress. J. Contemporary Chemical Industry, 39 (6): 723-725.
[8] Rudresh, B.M., et al. (2018) Influence of experimental parameters on friction and wear mechanisms of PA66/PTFE blend reinforced with glass fiber. J.Transactions of the Indian Institute of Metals.
[9] Yang, J.Y., et al.(2017) Study on the performance of carbon fiber reinforced polytetrafluoroethylene sealing material for oil free reciprocating compressor. J. Fluid Machinery, 45 (3): 6-10.
[10] Ying, L.X., Wang, X.H., Zhang, C.J., et al. (2017) Effect of PTFE content on microstructure and tribological properties of Cu-Sn coating. J.Advanced Materials Research,1142:173-177.
[11] Duan, C.J., Shao, M.C., Li, S., et al. (2018) Research progress of polyimide self-lubricating composite under extreme conditions. J. Chinese Science: Chemistry, 1-7.
[12] Jiang, Q., Wang, X., Zhu, Y., et al. (2014) Mechanical, electrical and thermal properties of aligned carbon nanotube/polyimide composites. J. Composites Part B Engineering, 56(2):408-412.
[13] Li, Z.L., Zhang, X.R., Wang, T.M., et al. (2016) Tribological properties of composite filled modified polyimide lubricating materials. J. Lubrication and Sealing, 41(10): 82-85.
[14] Zhu, M., Zhang, Z.Z., Wang, K., et al.(2004)Friction and wear properties of polytetrafluoroethylene and molybdenum disulfide filled polyimide composites. J.Journal of Tribology, 24 (6): 522-526.
[15] Liu, Y.B., Li, X.B., Sun, M.X., et al. (2016) Progress in preparation and application of PEEK coating. J. Material Protection, 049 (010): 78-82.
[16] Wang, Z., Yang, L.J., Wang ,T., et al. (2017)Study on PEEK based composite coating. J. Plastics Industry, 45 (03): 161-164+171.
[17] Yang, L.J., Wang, Z., Wang, T., (2017) Research and development of PEEK modification and coating. J. Plastics Industry, 45 (02): 15-20.
[18] Rasheva, Z., et al. (2010) A correlation between the tribological and mechanical properties of short carbon fibers reinforced PEEK materials with different fiber orientations. J.Tribology Int,43: 1430-1437.
[19] Zalaznik, M., Novak, S., et al. (2016) Tribological behaviour of a PEEK polymer containing solid MoS2 lubricants. J. Lubrication Science, 28(1):27-42.
[20] Mao, J.Y. (2014) Preparation and properties of new polyphenylene sulfide composite coating. D. Nanhua University.25-30.
[21] Cui, Y.X., (2017) Preparation of Tongyou microcapsule and self-healing and self-lubricating properties of epoxy resin coating. D. Northeast Petroleum University, 40-45.
[22] Yu, C.T., Chen, L., Li, H.X., et al. (2019) Study on properties of polyamide imide based lubricating coating modified by octaaminosesquioxane. J. Coating Industry, (5): 8-15.
[23] Beckford, S., Cai, J., Fleming, R.A., et al. (2016) The Effects of graphite filler on the tribological properties of polydopamine/PTFE coatings. J. Tribology Letters, 64(3):42.
[24] Patare, P.M., Lathkar, G.S. (2018) Optimization of glass fiber and MoS2 filled PTFE composites using non traditional optimization techniques. J. Materials Today:Proceedings, 5(2):7310-7319.
[25] Zhao, E.K., An, Y.L., Zhao, X.Q., et al. (2018) Research status of thermal spraying high temperature self lubricating coating. J. SurfaceTechnology, 47 (06): 104-111.
[26] Chen, J.M., Lu, X.W., Li, H.X., et al. (2014) Research progress of solid self-lubricating coating / coating materials with wide temperature range. J. Journal of Tribology, 34 (5): 592-600.
[27] Qu, M., Yao, Y., et al. (2017) Tribological study of polytetrafluoroethylene lubricant additives filled with Cu microparticles or SiO2 nanoparticles. J. Tribology, International, 110:57-65.
[28] Corni, I., Neumann, N., et al. (2009) Electrophoretic deposition of PEEK-nano alumina composite coatings on stainless steel. J. Surf Coat Technol, 203 (10) : 1349-1359.
[29] Ma, C., et al. (2014) Preparation of flexible amino fossil graphene/polyimide nanocomposite membrane by in situ polymerization. J. Journal of Lanzhou University of Technology, (06): 36-40.
[30] Zhao, G., et al. (2013) Friction and wear of fiber reinforced polyimide composites. J. Wear, (301):122-129.
[31] Wu, J., et al. (2010) Study of the splat-substrate interface for a PEEK coating plasma-sprayed onto aluminum substrates. J. Journal of Thermal Spray Technol, 19 (1-2) : 42-48.
[32] Long, C.G., He, L.P., Zhong, Z.H., (2006) Tribological study of PEEK composite materials. J. Polymer Materials Science and Engineering, 22 (4): 184-187.
[33] Fan, Z.G., Li, J., Yang, Z.D., et al. (2006) Study on physical properties of polytetrafluoroethylene coatings. J. Electroplating and Finishing, 25 (6): 24-26.
[34] Berman, D., Deshmukh, S.A., et al. (2015) Macroscale superlubricity enabled by graphene nanoscroll formation. J. Science, 348,1118-1122.
[35] Li, H., et al. (2017) Superlubricity between MoS2 monolayers. J. Adv. Mater, 29:1701474.
[36] Xia, Y., Mathis, T.S., Zhao, M.Q., et al. (2018) Thickness-independent capacitance of vertically aligned liquid-crystalline Mxenes. J. Nature, 557:409-412.
[37] Naguib, M., et al. (2014) Mxenes: A new family of 2D materials. J. Adv. Mater, 26:992-1005.
[38] Huang, W., (2019) Preparation and tribological properties of highly dispersed nano molybdenum disulfide. D. Huaibei Normal University, 2-6.
[39] Cui, J.B., Li, X., Mu, B., et al. (2018) Application and research progress of microcapsules in polymer materials. J. New chemical materials, 46 (S1): 5-9.