ISSN 2616-5880 Vol. 3, Issue 1: 23-30, DOI: 10.25236/AJMC.2022.030105

Research progress of modified carbon black used in rubber properties improvement

Yu Dang, Yanshan Liao, Chuan Yu, Siwei Cao

Queen Mary Engineering School, Northwestern Polytechnical University, Xi'an, 710000, China

Abstract: *Rubber is widely used as a common elastomeric material in various fields. However, the poor physical properties of rubber without filler reinforcement could not satisfy the needs in the practical applications. Consequently, various fillers were developed and used to enhance the mechanical properties of rubber. Carbon black, the most common reinforcing agent, can reinforce rubber through the uniform distribution of carbon black particles. However, it is prone to agglomerate due to the interaction between the carbon black aggregate in the actual production. Therefore, the modification of carbon black is required to achieve the optimum distribution. To deal with these problems, several modification methods have been investigated. In this review, the existing modification methods were sorted into four different types: graft modification, surface coating modification, oxidation modification, and surface adsorption modification. Furthermore, a comprehensive evaluation of these methods and the prospects of carbon black material modification were presented.*

Keywords: *Carbon black, Modification methods, Rubber reinforcement*

1. Introduction of rubber

Rubber is a type of elastomer material which plays a significant role in many industrial applications such as tyre and sealing material. It has good mechanical properties like very high elasticity, relatively low stiffness with Young's modulus around 10^5~10^7 Pa, and can perform large recoverable deformation before a break at about 500% ~1000% [1]. In industrial applications, many other mechanical properties including tensile strength, wear strength, hardness, friction resistance, and rolling resistance must be adapted by various processes to get the expected performance.

The academic research on rubber can be traced back to the early 18th century while the industrial application began around the 1820s when British factories produced natural rubber-based raincoats [2]. The rubber in this period lacked the necessary stiffness, so its application was quite limited. This situation lasted until 1839 when Goodyear invented the vulcanization method of rubber, which greatly improved the mechanical properties of rubber [2]. However, although vulcanized rubber can display a lot of mechanical performance, it remains weak in many applications. In order to further improve the strength and many other mechanical properties of rubber materials, reinforcing agents are introduced into the rubber system. Carbon black is one of the most common and effective agents used in rubber development [3]. The academic research on carbon black reinforced rubber began at the beginning of the 20th century. In order to improve the reinforcement performance of carbon black, people have studied a variety of modification methods.

2. General information of carbon black

Carbon black is a black powdery substance produced by incomplete combustion of hydrocarbons or heated solutions in the gas phase. Under different process conditions, various carbon black products with different properties can be obtained. Due to good weather resistance, coloring ability, filling ability, electrical conductivity, aging resistance and chemical stability, carbon black is one of the important industrial raw materials and the world's largest amount of black colorant, mainly used in the manufacture of tires, plastics, mechanical rubber products, printing ink, toner, insulating wires and cable and other fields. As the most traditional rubber reinforcement, carbon black can not only reduce the amount of rubber but also improve the processability properties, the application performance and the service life of rubber, which has a great relationship with the intrinsic properties of carbon black [4]. The primary structure is a carbon black aggregate which is the smallest unit of carbon black. Agglomerate, a space network structure formed by van der Waals forces between the carbon black aggregates, is the secondary structure of carbon black, which is not strong and is easy to be crushed into aggregates when mixed with rubber [4]. The specific surface area (or the particle size), the structure (primary particles and 3D branched cluster), and the surface activity are three basic characteristics of carbon black. The surface area can be calculated by a variety of adsorption methods [5], which affects the blackness and dispersion of carbon black when mixed with rubber. Generally speaking, the smaller the particle size, the higher the blackness of carbon black. The structure of carbon black is expressed by the degree of aggregation, which is measured by the oil absorption value. The higher the oil absorption value, the higher the structure of carbon black. The surface activity is corresponding with the groups on the surface, playing an important role in the filler-matrix and filler-filler interaction.

The reinforcing mechanism of carbon black can be summarized as surface adsorption layer theory and molecular chain sliding theory. The theory of surface adsorption layer suggests that the addition of vulcanizing agent and carbon black makes the rubber form a micro polynomial heterogeneous structure with different properties. The molecular chain sliding theory proposes that different rubber chains adsorbed on the carbon black surfaces are stretched under stress to achieve stress distribution [6].

However, carbon black has a large specific surface area and a strong intermolecular force, which makes it easy for carbon black to agglomerate into large particles in the dispersion medium during processing, and it is difficult to disperse stably in the matrix, which directly affects the quality of carbon black products and is not conducive to the optimization of rubber mechanical properties. Therefore, improving the dispersion of carbon black is of great significance to protect the environment and improve the properties of rubber.

3. Modification of carbon black

To obtain a carbon black/rubber composite with optimized mechanical properties, one possible method is to modify the surface of carbon black to reduce the attraction between carbon black particles or strengthen the interaction between rubber and carbon black. In this way, an optimal dispersion of the carbon black in the rubber can be achieved. Since carbon black has been used in the rubber industry for a long time, many modification methods have already been applied to the surface treatment of carbon black. Four main methods will be discussed in this section below.

3.1 Graft modification of carbon black

Grafting modification is a very effective method to improve the reinforcement performance of carbon black in rubber systems. In this process, polymer molecules are grafted onto the surface of carbon black through a chemical reaction [7,8]. By attaching polymer molecules, the steric hindrance between modified carbon black prevents the formation of the filler network and increases the dispersion of carbon black in the rubber system [8]. The attached polymer molecules generally also have great interaction with the rubber system that the compatibility between the carbon black and the rubber is therefore improved simultaneously [8].

The mechanism of this "grafting reaction" is slightly different in each specific case and there are mainly three categories of graft-modification mechanism: grafting onto carbon black, grafting from carbon black and reaction of carbon black with functional polymers [9]. In the "grafting onto carbon black" mechanism, the carbon black acts like a "free radical scavenger": the growing polymer radical, which could also be a growing polymer cation or anion, can be captured by some functional groups on the carbon black surface and become deactivated [9]. For the "grafting from carbon black" mechanism, some initiating groups are introduced onto the carbon black first, which then contributes to the initiation of the polymerization process and achieves the grafting structure [9]. For the final mechanism, the "reaction of carbon black with functional polymer", the grafting reaction does not happen during the polymerization process. Instead, grafting is achieved by the combination of carbon black and complete polymer molecules [9]. Such combinations can be achieved in two ways: either by using carbon black with reactive functional groups, such as isocyanate group or acyl chloride groups or by using polymers with similar reactive end-groups [9]. These mechanisms have different strengths and drawbacks. The "grafting onto" mechanism usually can only give a relatively low grafting degree with approximately less than 10% polymers can be attached on the carbon black surface [9]. The "grafting from" mechanism can achieve a higher grafting degree but the amount of grafted polymer chain, in this case, is difficult to control. For the "reaction with functional polymer" mechanisms, the grafting amount is easy to control. This mechanism is not a polymerization process, and the polymer can have a well-defined chemical structure and molecular weight. However, these methods are very similar, and all create modified carbon

ISSN 2616-5880 Vol. 3, Issue 1: 23-30, DOI: 10.25236/AJMC.2022.030105

blacks with the corresponding chemical attachment of the surface of the material molecule.

In practice, many researchers have applied this grafting modification method to the carbon black reinforced rubber systems and achieved good performance. Many polymers are very suitable for this kind of grafting modification. Fu et al. [10] tried to graft polyethylene glycol 400 (PEG 400) onto the surface of carbon black by the in-situ liquid method. The dispersion of modified carbon black in the rubber system was good, and the interaction between filler and rubber was also enhanced after modification. Based on the characterization data, the tensile strength and tear strength of the rubber were increased by 6.1 MPa and 19.5 KN/m, respectively and the rubber also achieved higher abrasion resistance. Similar to the PEG modification approach, Han et al. [11] attempted to use hyper-branched poly (2-hydroxypropane-1,2,3-tricarboxylic acid) (HBP) to conduct this grafting modification. The difference in this modification procedure was that, before grafting the HBP, a pretreatment was conducted where a great number of carboxyl groups were introduced on the carbon black surface. After this step, the polymerization process occurred and the formed polymers, HBP, were grafted onto the carbon black surface with the help of those carboxyl groups. The characterization results showed that the dispersion of the modified carbon black was indeed significantly improved and, very similar to the “PEG modification” example, when the filler content was controlled to be 30 parts per hundreds of rubber (phr), the tensile strength and tear strength of the rubber system was found to be increased by 6.2 MPa and 18,7 KN/m, respectively. An even better modification result was achieved by Li et al. [12] who grafted PMMA on the carbon black surface. The process also started with the MMA monomer, using potassium persulfate as the initiator. After modification, the tensile strength and tear strength of the rubber system were increased by about 9 MPa and 35 KN/m respectively. At the same time, the rubber system also showed better aging resistant performances. In addition to such common polymers, another type of agent which is frequently used in the graft modification is the silane coupling agent. Song et al. [13] used 3-(Trimethoxysilyl) propyl methacrylate (MPS) to do the graft modification. The procedure followed the “graft from carbon black” mechanism where the polymerization of MPS was initiated on the carbon black surface and resulted in many grafted silane coupling agents (PMPS) on the carbon black surface. The characterization results demonstrated that the silane coupling agent can significantly improve the dispersion of carbon black. The modified carbon black also increased the stiffness, strain at failure and deformation recovery degree of the rubber system. Xie et al. [14] investigated a similar method using another silane coupling agent TESPT. After modification, the tensile strength and tear strength of the rubber had a tiny increase while its loss factor and heat build-up showed a remarkable decrease. In the above example, there are always some new compounds introduced into the rubber system, which can be a common polymer or silane coupling agent. In addition to these methods, some researchers even try to directly use the rubber molecules in the rubber system to modify the carbon black contained therein. Xu et al. [15] grafted carbon black with natural rubber and enhanced natural rubber system with modified carbon black. They grafted natural rubber compounds by a solid-state method. SEM results showed that there was no filler network in the rubber system and the modified carbon black was highly uniformly dispersed in the system. The tensile strength of the rubber system with modified carbon black was about 3 MPa higher than that of the rubber system with unmodified carbon black and the tear strength was also increased by 18 KN/m. In addition to the improved static mechanical properties, the rubber did not show the Payne effect during the dynamic testing and its curing rate and density were also significantly improved.

Based on these previous experiments, it can be concluded that numerous different compounds can be used to modify carbon black and they can improve the mechanical properties of the reinforced rubber system to a certain extent [10~15]. In some cases, it is also found that these grafted compounds have a significant effect on improving the dynamic properties and curing properties of the rubber system [12~15].

3.2 The surface adsorption modification of carbon black

The surface adsorption modification of carbon black can also meet the requirements of uniform distribution of carbon black in rubber materials. Due to the long-term development of carbon black / rubber materials, the reinforcement mechanism has been further studied and it is concluded that the physical interaction between rubber and carbon black is important [16]. In the past two decades, Park and Brendle [17] found that the nonpolar component of the surface energy of the filler is a predominant factor in its adsorption ability. Then, Park and Kim [16] used a base to treat the surface of carbon black and the result showed an even distribution of carbon black. In this experiment, the surface energy of carbon black was decreased due to the modification of the base. Besides, Park et al. [18] continuously used oxygen plasma to deal with the surface of carbon black and found that the tearing energy of carbon

ISSN 2616-5880 Vol. 3, Issue 1: 23-30, DOI: 10.25236/AJMC.2022.030105

black/NBR increased. Through this method, not only the surface energy of carbon black was decreased, but also due to the appearance of the oxygen-containing groups which can interact with the polar NBR, the distribution of carbon black can be improved.

In addition, carbon black can be modified by adding carbon black dispersant which can be adsorbed on the surface of carbon black to achieve uniform dispersion. There are various types of carbon black dispersants, mainly involving low molecular dispersants, high molecular dispersants, and mixed dispersants.

The low molecular dispersant is a kind of surfactant, which is used to prepare the carbon black aqueous dispersion system. Surfactant is adsorbed on the carbon black surface in Langmuir form. Thus, the surface adsorption capacity is weakened. However, due to the extremely weak spatial resistance of low molecular dispersants, this will lead to more unstable dispersion systems. Therefore, in view of the high spatial resistance of polymer dispersants, it has attracted more attention in aqueous carbon black systems. The principle of polymer dispersant is that the anchoring end adsorbed on the surface of carbon black will produce responding spatial resistance. Additionally, the mixing between different kinds of carbon black dispersants is also a hot spot in the research on surface modification of carbon black. The principle of the mixed carbon black dispersants is mainly mixing between dispersants. The modification of carbon black by this method is simple and requires low experimental conditions. The only difficulty is choosing different dispersant combinations. The synthesis of special dispersants for carbon black has always been one of the hot spots in the research of carbon black dispersion.

3.3 Oxidation modification of carbon black

The oxidation modification technology of carbon black has been relatively mature. The surface oxidation of carbon black introduces oxygen-containing functional groups to change the surface polarity and the compatibility with the matrix, mainly including gas-phase oxidation, liquid-phase oxidation, plasma oxidation and catalytic oxidation.

The gas-phase oxidation method uses oxygen, air, ozone, nitrogen oxides and other oxidizing gases as oxidants to modify the surface of carbon black. Using weak oxidizing gases such as air and oxygen, the reaction temperature is high, resulting in high energy consumption and decomposition of oxygen-containing groups on the surface [19]. Nitrogen oxide gas has the disadvantages of the limited source of raw materials, high cost and environmental pollution. Ozone is one of the most widely used gases. It has the advantages of mild reaction conditions, wide gas source, low cost, low energy consumption and high oxidation efficiency. Ozone oxidation methods can be divided into air oxidation methods and fluidized bed oxidation methods according to different operations. The high-efficient fluidized bed reactor is one of the main research directions in the field of ozone oxidation [19]. Sutherland et al. [20] used a fluidized bed reactor to conduct ozone treatment on the surface of carbon black and concluded that the surface oxygen level was proportional to the total amount of ozone and the acidity of the carbon black surface. The results of XPS spectrum and FTIR spectrum indicated that the surface oxygen was in the form of the carboxylic acid group.

The liquid phase oxidation method is to generate oxygen-containing functional groups on the surface of carbon black through the redox reaction between carbon black and strong oxidant in the aqueous solution. As the earliest industrial surface oxidation modification method of carbon black, there are many related literature reports. The oxidants used are generally strong oxidizing solutions, such as hydrogen peroxide, sulfuric acid, nitric acid, saturated ammonium persulfate, perchloric acid, sodium hypochlorite and potassium permanganate solution, etc [21,22]. The modification greatly improves the oxygen-containing functional groups on the surface of carbon black, which is superior to gas-phase oxidation.

Catalytic oxidation modification of carbon black uses metal chloride ($TiCl_4$, $CrOCl_4$, etc.), gold oxygenates (Cr_2O_3, CuO, etc.) or nitrogen oxides as catalysts for catalytic oxidation [19]. Multiple research results have shown that in a certain gas atmosphere, catalyst oxidation of carbon black can improve the content of oxygen-containing groups on the surface. However, too high oxidation reaction temperature leads to the reduction of oxidizing efficiency and decomposition of oxygen-containing groups to generate CO_2 and CO gas, resulting in low efficiency of modification and a low concentration of surface oxygen-containing functional groups. Neeft et al. [23] confirmed that the addition of catalysts including PbO, Co_3O_4, V_2O_5 and Ag_2O can increase by more than 100 times when the powder catalyst has the best contact with carbon black at 656 K in Ar. Uchisawa et al. [24] loaded Pt precursors on SiO_2, Al_2O_3 and ZrO_2 as catalysts for catalytic oxidation of carbon black, among which Pt/SiO2 prepared had the best performance on the oxidation activity. This method is still under laboratory development, and further research on efficient and environmentally friendly catalysts is needed to achieve industrialization.

In oxygen plasma treatment, the polar groups are introduced into the surface of carbon black in the discharge process. Three main oxygen plasma methods including microwave plasma, radio frequency (RF) plasma and ARC plasma are explored [18,25,26]. This treatment has four principal advantages: (1) The oxidation reaction only occurs on the carbon black surfaces because the plasma first contacts the surface of carbon black with no change in the bulk of carbon black. (2) A variety of atmospheres including oxidation, inert and reductive atmospheres can be used [27]. (3) The airflow temperature in the oxidation process is relatively mild and the oxygen-containing functional groups on the surface of carbon black will not decompose into gases such as CO and CO_2 due to high temperature [19]. (4) No waste generation and low modification cost.

Li et al. [26] conducted RF plasma treatment with an input power of 15 W under an oxygen pressure of 2. 00 MPa. The amount of adsorbed water was proportional to the plasma treatment time, indicating that the surface had changed from hydrophobic to hydrophilic. Li et al. [28] used the RF method and dielectric barrier discharge plasma (DBD) respectively. Through comparing the properties of carbon black by the two kinds of treatment, DBD is superior to RF was concluded, and the carbon black after plasma treatment had good properties with more oxygen-containing functional groups, increased volatilization, increased BET, and significantly improved dispersion stability. Park et al. [18] varied treatment time from 0 to 30 minutes with generating the RF treatment as 13.56 MHz. It was inferred from the XPS spectrum that oxygen plasma treatment produced active carbon radicals from the hydrocarbon framework, which generated a reaction when exposed to oxygen to increase the oxygen-containing functional groups on the carbon black surface. The contents of C=O, O-C=O, COOH, and other functional groups on the surface of carbon black increased within 0 to 20 min, indicating that oxygen polar groups would be generated by oxygen plasma treatment, while the concentration of oxygen functional groups decreased after 20 min, possibly because the plasma began to remove weak or unstable bonds after prolonged treatment time. Cao et al. [29] used the RF method under an oxygen atmosphere with different power and then the modified carbon black was disposed into moisture dispersion to measure its natural sedimentation rate. The results showed that the dispersion stability of carbon black in water changes regularly, and the dispersion stability in moisture dispersion had been greatly improved. Although the plasma oxidation method has great development prospects in industrial production, the uniform oxidation of the surface and the reduction of energy consumption are still the focus of research at present.

3.4 Coating modification of carbon black

The uniform dispersion of carbon black is usually difficult to be achieved as a stable dispersion system only by the external action of the dispersing mechanical equipment. And surface coating technology is also a feasible method to accomplish this goal to strengthen the mechanical properties of the rubber. Besides, the combination of the various fillers with the different properties can have a synergistic effect on the properties of the polymer and further improve the mechanical properties of the rubber through the appropriate combination techniques. According to the development of coating method, there already exists solid-phase, liquid-phase and gas-phase coating methods. Each of the three methods has its advantages and disadvantages. They have been developed in different regions due to the different needs. Generally, thermoset materials are the most common coating agent for carbon black. Qian et al. [30] combined carbon black with silica through a pyrolysis process and gained the product as silica carbon black (SiCB). Then this material was further coated with phenolic formaldehyde resin (PF) which is a kind of resin. As it was embedded into rubber, the result demonstrated that the tensile strength increased a lot. And the final rubber composite achieved a high performance through the improved interfacial interaction. Besides, Ghasemi-Kahrizsangi et al. [31] used epoxy to coat the carbon black particles. Due to the appearance of aromatic functional groups in epoxy, the anti-UV ability of the composite was improved. Also, by the method of incorporating carbon black nanoparticles into epoxy, a stable and even distribution was achieved.

4. Evaluation of different kinds of carbon modification

For the graft modification method, a great amount of research has been conducted to investigate its mechanism and modification performance. In recent years, lots of chemicals have been used and some of them have presented excellent behavior. However, one problem of this method is that the grafting degree could be difficult to control in some procedures which may lead to unreliable modification performance. Finding reliable methods to control the structure and the molecular weight of the grafted polymer should be a potential research direction for future development.

The surface adsorption modification of carbon black is generally carried out with different types of solutions for carbon black, such as neutral alkali solutions, different surfactants, etc. Through the treatment of these liquids, the surface energy of carbon black is reduced or the force between carbon black and rubber is enhanced, so that the primary particles of carbon black can be more easily dispersed in rubber uniformly. Therefore, better mechanical and processing properties of rubber materials can be achieved. Further, this modification method is relatively simple, together with low energy consumption, and can adapt to the requirements of industrial mass production. In addition, the modified liquid has less volatility which indicates lower pollution. Therefore, it is more in line with the requirements of green production, but the modification effect is relatively poor.

The oxidation method is used to change the surface polarity of carbon black and its compatibility with the matrix by introducing oxygen-containing functional groups which are relatively mature. Liquid-phase oxidation method is the earliest development of the carbon black oxidation modification method, there have been a variety of solutions that can be used, and the modification performance is better than the use of the gas-phase oxidation method. With producing waste in the liquid-phase method, further research should be studied. The catalytic oxidation method is still at the laboratory level, while the catalysts based on metal materials are costly and energy-intensive, which is not conducive to industrial production. In contrast, the plasma oxidation method has great prospects for industrial production, with low reaction environment requirements, mild reaction temperature without decomposition of oxygen-containing functional groups, no waste generation, and lower cost than catalytic oxidation, but the ways to make the carbon black oxidized uniformly and reduce the reduction of energy consumption are still in the development.

The surface coating of carbon black is utilizing physical or chemical methods to envelop the surface of the particles according to the need. By using the different substances to coat the surface, the distribution of carbon black particles can be improved. In recent years, surface coating technology has been greatly developed, which is mainly divided into solid-phase coating, liquid-phase coating, and gas-phase coating. The solid phase coating method mainly uses mechanical mixing methods, such as extrusion, which is easy to control the reaction process with the processing time. Also, it is possible for a continuous mass production. However, due to the strict requirements for particle size, this method is only applicable to micron-sized particles. The liquid phase wrapping method is mainly a chemical method, which uses the chemical reaction in the wet environment to form the modified carbon black. The carbon black particles prepared by this method have higher purity, good chemical uniformity, and a narrow particle size distribution. However, more chemical reagents are involved in the actual operation engineering, which may have some impact on the environment. The vapor phase coating method is mainly used to achieve the coating of carbon black by chemical vapor deposition. This method can precisely control the formation of a specific thickness of the carbon black coating layer, but compared with other methods, this method is relatively high energy-consuming, which is not conducive to its application in industrial rubber production.

5. Conclusion

To summarize, carbon black is a typical reinforcement filler that is widely used to improve the mechanical properties of rubber. However, it is very easy to be agglomerated into a large particle during processing which will lead to quite limited dispersion of carbon black in the rubber system and therefore restrict the mechanical performance of the reinforced rubber. To solve this problem, many methods have been used to modify the carbon black surface to reduce the interaction between the carbon black. Different modification methods have different features: Some methods are very simple but only show limited improvement; some can achieve very accurate control but have relatively intensive energy consumption. Some show excellent performance in the laboratory but still cannot be applied to mass industrial production. The most ideal method should show relatively good and stable improvement performance with low energy consumption making it suitable for industrial application. At the same time, too much pollution shall not be generated during the treatment process to minimize the negative environmental impact. To find such a mature method, we still need to do a lot of research work, which is a very practical and promising research direction in the field of materials on effect is relatively poor.

ISSN 2616-5880 Vol. 3, Issue 1: 23-30, DOI: 10.25236/AJMC.2022.030105

References

[1] Treloar L. The physics of rubber elasticity[M]. Oxford: Clarendon Pr., 2009.
[2] Hurley P E. History of natural rubber[J]. Journal of Macromolecular Science—Chemistry, 1981, 15(7): 1279-1287.
[3] Robertson C G, Hardman N J. Nature of carbon black reinforcement of rubber: Perspective on the original polymer nanocomposite[J]. Polymers, 2021, 13(4): 538.
[4] Nakajima N. Knowledge gap in characterization of reinforcing fillers, structure-processability relation of agglomerates[J]. Journal of Elastomers & Plastics, 2002, 34(4): 323-334.
[5] MAGEE R W. Evaluation of the External Surface Area of Carbon Black by Nitrogen Adsorption[J/OL]. Rubber Chemistry and Technology, 1995, 68(4): 590-600[2022-06-02].
[6] FRÖHLICH J, NIEDERMEIER W, LUGINSLAND H D. The effect of filler–filler and filler–elastomer interaction on rubber reinforcement[J/OL]. Composites Part A: Applied Science and Manufacturing, 2005, 36(4): 449-460. DOI:10.1016/j.compositesa.2004.10.004.
[7] Wang X. Synthesis of Multifunctional Silane Coupling Agent and Its Application in Carbon Black and Silica Reinforced Isoprene Rubber Composites[D]. Xiangtan University, 2021.
[8] Cen L, Zhou Y, Chen F. Modification of Carbon Black and its Application to Rubber[J]. Special Purpose Rubber Products, 2007, 28(4): 7-11.
[9] Tsubokawa N. Functionalization of carbon black by surface grafting of polymers[J]. Progress in Polymer science, 1992, 17(3): 417-470.
[10] Fu W, Liu A, Yang J. Effects of In-Situ Grafting-Modified Carbon Black on Properties of Natural Rubber[J]. Journal of South China University of Technology: Natural Science Edition, 2014, 42(6):7.
[11] Han F, Zhang Z, Ma T, et al. Preparation and mechanical properties of water-dispersible hyperbranched polymer grafted carbon black/natural rubber composites by latex blending method[J]. Polymers for Advanced Technologies, 2022, 33(1): 368-379.
[12] Li W, Luo Y, Jia D. Preparation of Carbon Black-containing-NR Composite by Monomer in-Situ Grafting in Latex[J]. Natural Science Journal of Xiangtan University, 2004, 26(4): 63-66.
[13] Song P, Wang G, Zhang Y. Preparation and performance of graphene/carbon black silicone rubber composites used for highly sensitive and flexible strain sensors[J]. Sensors and Actuators A: Physical, 2021, 323: 112659.
[14] Xie F, Li Y, Li J, et al. Influence of Modification of Carbon Black with Coupling Agent on Properties of Rubber[J]. China Rubber Industry, 1996, 43(6): 335-338.
[15] Xu H, Han J, Fang L, et al. Effect of grafted carbon black on properties of vulcanized natural rubber[J]. Polymer Bulletin, 2007, 58(5): 951-962.
[16] Park S J, Kim J S. Role of chemically modified carbon black surfaces in enhancing interfacial adhesion between carbon black and rubber in a composite system[J]. Journal of colloid and interface science, 2000, 232(2): 311-316.
[17] Park S J, Brendle M. London dispersive component of the surface free energy and surface enthalpy[J]. Journal of colloid and interface science, 1997, 188(2): 336-339.
[18] Park S J, Cho K S, Ryu S K. Filler–elastomer interactions: influence of oxygen plasma treatment on surface and mechanical properties of carbon black/rubber composites [J]. Carbon, 2003, 41(7): 1437-1442.
[19] Li W, Wang Y, Gao M, et al. Research Progress for Oxidation Modification of Carbon Black[J]. DYESTUFFS AND COLORATION,2017,04:13-17.
[20] Sutherland I, Sheng E, Bradley R, et al. Effects of ozone oxidation on carbon black surfaces[J]. Journal of Materials Science, 1996, 31(21): 5651-5655.
[21] Beck N, Meech S, Norman P, et al. Characterisation of surface oxides on carbon and their influence on dynamic adsorption[J]. Carbon, 2002, 40(4): 531-540.
[22] Trawczynski J, Suppan S, Sayag C, et al. Surface acidity of the activated CBC[J]. Fuel Processing Technology, 2002, 77-78: 317-324.
[23] Neeft J. Catalytic oxidation of carbon black--I. Activity of catalysts and classification of oxidation profiles[J]. Fuel, 1998, 77(3): 111-119.
[24] OI Uchisawa J, Obuchi A, Zhao Z, et al. Carbon oxidation with platinum supported catalysts[J]. Applied Catalysis B: Environmental, 1998, 18(3-4): L183-L187.
[25] DE TORRE L E Cascarini, BOTTANI E J, MARTÍNEZ-ALONSO A, et al. Effects of oxygen plasma treatment on the surface of graphitized carbon black[J/OL]. Carbon, 1998, 36(3): 277-282[2022-06-02].
[26] LI X, HORITA K. Electrochemical characterization of carbon black subjected to RF oxygen plasma[J/OL]. Carbon, 2000, 38(1): 133-138[2020-05-04]. DOI: 10.1016/s0008-6223(99)00108-6.
[27] FRYSZ C A, CHUNG D D L. Improving the electrochemical behavior of carbon black and carbon filaments by oxidation[J/OL]. Carbon, 1997, 35(8): 1111-1127[2020-05-18].

ISSN 2616-5880 Vol. 3, Issue 1: 23-30, DOI: 10.25236/AJMC.2022.030105

[28] Lanying L, Study on Carbon Black Oxidized by Plasma Grafting Antitymour Etoposide (VP-16) [D]. Chengdu: Sichuan University, 2005.
[29] Shuhua C,Zhijun D,Li S,Plasma Oxygen Treatment of Carbon Black Powder and Its Dispersibility in Water[J].Journal of Donghua University (Nature Science), 2009 (02): 186 —189,193. Plasma Oxygen Treatment of Carbon Black Powder and Its Dispersibility in Water
[30] Qian M, Huang W, Wang J, et al. Surface treatment effects on the mechanical properties of silica carbon black reinforced natural rubber/butadiene rubber composites[J]. Polymers, 2019, 11(11): 1763.
[31] Ghasemi-Kahrizsangi A, Neshati J, Shariatpanahi H, et al. Improving the UV degradation resistance of epoxy coatings using modified carbon black nanoparticles[J]. Progress in Organic Coatings, 2015, 85: 199-207.