Study on Mechanical Properties of Natural Rubber by Carbon Black/Graphene/White Carbon Black

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Abstract. Graphene (GE) and white carbon black (SiO2) were added to natural rubber (NR) to partially replace carbon black (CB). The effects of different filling ratios of CB/GE/SiO2 on the mechanical properties of NR were investigated. The data were processed by orthogonal experiment. The results showed that when the mass fraction of CB was 41g, the mass fraction of GE was 4g, and the mass fraction of SiO2 was 1g, the maximum true strain in the mechanical properties of NR was 139.8%. The maximum true stress is 85.695 MPa, and it is indicated that 41g CB, 4 g GE, and 1 g SiO2 are added to the NR as the optimum filling ratio.

Key words: Graphene; Carbon black; White carbon black; Natural rubber; Mechanical properties; Stress strain.

1. Introduction

The mechanical properties of pure natural rubber (NR) are poor, and the mechanical properties of NR are improved by filling the reinforcing filler. Carbon black and white carbon black are two reinforcing fillers in the rubber industry. Both fillers can form aggregates in rubber compounds [1, 2, 3, 4]. Due to their different surface characteristics, the mechanical properties are different, but the overall interaction has a good improvement on the mechanical properties of NR [5, 6]. The filler-filler interaction of carbon black is mainly produced by relatively weak van der Waals forces, which are easily destroyed during the mixing process [7, 8, 9]; In addition to Van der Waals force and other physical interactions, the agglomeration of silica has hydrogen bonding, and the filler-filler interaction is stronger. Carbon black/white carbon black has poor compatibility between molecules in the rubber. The addition of graphene can enhance the compatibility between molecules to some extent, improve the mechanical properties of rubber. Graphene itself has excellent mechanical properties [10, 11]. For example, the original graphene prepared by vapor phase deposition has an elastic modulus of 1 TPa and an ultimate strength of 130 GPa [12]. All three fillers can enhance the mechanical properties of NR [13, 14, 15], but the ratio of the three of them has not been studied by scholars.

In this paper, some carbon black were replaced by graphene and white carbon black, and three kinds of fillers were simultaneously added into natural rubber. The effects of different filling ratios of carbon black/graphene/white carbon black on the vulcanization characteristics and mechanical properties of NR were studied.
2. Experimental part

2.1. Raw Materials

Natural rubber (NR), grade 3L, Dongguan Kunhe Plastic Chemical Co., Ltd. products. Carbon black, grade N330, Tianjin Yihuachang New Material Technology Co., Ltd. products. White carbon black, DuPont chemical business products in Jinshui District, Zhengzhou City. Zinc oxide content of 99.7%, accelerator M (MBT), anti-aging agent 4020NA and stearic acid 1801, Shijiazhuang Youlian Chemical Co., Ltd. products. Silane coupling agent, brand SI-69, Dongguan Changping Yuxin Plastics Business Department. Graphene, liquid phase stripping method, product of the production and research base of Chongwen Avenue, High-tech Zone, Jining City, Shandong Province. Sulfur, Jiangsu Huaxing New Material Technology Co., Ltd.

2.2. Sample Preparation

Basic formula: NR100 parts (mass parts, the same below), zinc oxide 5 parts, stearic acid (1801) 2 parts, accelerator M (MBT) 1 part, antioxidant (4020NA) 2 parts, sulfur 2.5 parts, silane 3 parts of coupling agent (Si69), carbon black / graphene / white carbon black are 47/1/1, 47/2/2, 47/3/3, 47/4/4, 44/1/2, respectively. 44/2/1, 44/3/4, 44/4/3, 41/1/3, 41/2/4, 41/3/1, 41/4/2, 38/1/4, 38/2/3, 38/3/2, 38/4/1.

Mixing rubber and vulcanize: Place the NR at room temperature on the machine and roll it evenly. The mixture was prepared in the order of zinc oxide, stearic acid, accelerator M (MBT), anti-aging agent (4020NA), carbon black, the mixture was prepared by adding the graphene, white carbon black and sulfur. The mixture was allowed to stand at room temperature for 18 h, and then the vulcanization curve was measured at 150 °C using a non-rotor vulcanizer to obtain the vulcanization time (Tc90). It was corrected to obtain a vulcanization time of 1.3*Tc90, and the vulcanize was Vulcanized on a flat vulcanizing machine to obtain a carbon black/graphene/white carbon black mass ratio of 47/1/1, 47/2/2, 47/3/3, 47/4/4, 44/1/2, 44/2/1, 44/3/4, 44/4/3, 41/1/3, 41/2/4, 41/3/1, 41/4/2, 38/1/4, 38/2/3, 38/3/2, 38/4/1, marked as 1#, 2#, 3#, 4#, 5#, 6#, 7#, 8#, 9#, 10#, 11#, 12#, 13#, 14#, 15#, and 16#.

2.3. Analysis and Testing

Adopting X(SK)-160 open-type rubber (plastic) machine produced by Shanghai Double Wing Rubber Machinery Co., Ltd. with the roller speed ratio of 1:1.35; using XLB type flat vulcanizing machine produced by Qingdao Yadong Rubber Machinery Co., Ltd. The AI-7000M tensile testing machine produced by the high-speed rail testing instrument Co., Ltd. was used to measure the tensile properties according to GB/T 529-2008; the M2000-AN type produced by the high-speed rail testing instrument Co., Ltd. The vulcanization characteristic curve was tested by a rotor fluidizer under the test condition of 150 °C × 30 min; the morphology was observed by a SU8010 cold field emission scanning electron microscope (SEM) manufactured by Hitachi, Ltd., Japan.

3. Result and Discussion

3.1. Vulcanization characteristics

As can be seen from Table 1, the maximum torque (MH), minimum torque (ML), and MH of the composite rubber increase when the parts of GE/SiO2 increase when the carbon black parts are 47 g and 44 g. The difference in ML (ΔM) generally shows a gradual increase. This may be because the addition of GE/SiO2 has a greater restriction and hindrance to the movement of rubber molecular chains, which is manifested by an increase in MH and ML, and an increase in ΔM is due to the small amount of GE/SiO2 particles. The diameter size makes it play the role of physical cross-linking point when dispersed in the rubber molecular chain, which leads to the improvement of the cross-linking degree of the system, thus improving the mechanical properties of the NR rubber compound.

When the mass fraction of graphene reaches 4 g of the maximum fraction and when the fraction of CB/SiO2 gradually decreases, the vulcanization time and the scorch time tend to increase first and then decrease. This may be related to the specific surface area of carbon black and white carbon black.
respectively. The smaller the specific surface area is, the faster the vulcanization rate of the rubber compound and the shorter the vulcanization time will be, which in turn affects the mechanical properties of the NR vulcanizate.

Table 1. Curing properties of CB/GE/SiO$_2$ for NR mixture.

| CB/GE/SiO$_2$ | MH/ (dN • m) | ML/ (dN • m) | (MH- ML)/ (dN • m) | Tc90/min | Ts2/min |
|----------------|--------------|--------------|-------------------|----------|---------|
| 1#             | 32.04        | 0.55         | 11.04             | 9.86     | 2.62    |
| 2#             | 29.03        | 0.34         | 9.10              | 10.62    | 2.03    |
| 3#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 4#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 5#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 6#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 7#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 8#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 9#             | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 10#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 11#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 12#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 13#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 14#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 15#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |
| 16#            | 30.73        | 0.61         | 9.91              | 2.25     | 1.79    |

CB: carbon black; GE: graphene; SiO2: white carbon black; MH: maximum torque; ML: minimum torque; Tc90: vulcanization time; Ts2: scorch time.

As can be seen from Figure 1, when the mass fraction of CB is 47g, the maximum torque (MH) is the largest group of all the compounds. While MH is the characterization of the stiffness or shear modulus of the rubber when it is completely vulcanized and minimum torque (ML) is the characterization of the initial modulus of the unvulcanized rubber. After adding GE/SiO2, the ML basically shows an upward trend, indicating that GE/SiO2 has a greater effect on the initial modulus of the rubber mixture than CB. Probably because the ability of CB to adsorb rubber molecular chains is weaker than that of GE/SiO2, which in turn affects the mechanical properties of NR vulcanizate.
3.2. Mechanical Properties
In this paper, orthogonal test design method was used to study the effect of different filling ratios of CB/GE/SiO2 on the mechanical properties of NR. Orthogonal arrangement of experiments can save time and reduce costs. Through a few representative experiments, the influence of each factor on the results is ascertained, and the order of factors is determined according to the size of the influence, and the optimal combination of parameters is found. The comprehensive balance method designed by multi-index orthogonal experiment can find the optimal conditions of single index, and balance these conditions to find out the production conditions that take into account the various indicators.

In this paper, according to the orthogonal test to improve the mechanical properties of rubber, the tensile strength and elongation at break are the test indicators. CB/GE/SiO2 are three factors, which are represented by A, B and C respectively. For the four levels, the number of designed factors is shown in Table 2. The orthogonal test plan and test results are shown in Table 3.

Table 2. Factor levels.

| Level | CB (g) | GE (g) | SiO2 (g) |
|-------|--------|--------|----------|
| A     | 1      | 1      | 1        |
| 2     | 44     | 2      | 1        |
| 3     | 41     | 3      | 2        |
| 4     | 38     | 4      | 4        |

Table 3. Orthogonal experimental scheme and experimental results.

| Experiment number | CB(A) (g) | GE(B) (g) | SiO2(C) (g) | Tensile strength (MPa) | Elongation at break (%) |
|-------------------|-----------|-----------|-------------|------------------------|-------------------------|
| 1                 | 1(47)     | 1         | 1           | 20.467                 | 295.116                 |
| 2                 | 1         | 2         | 2           | 15.362                 | 247.755                 |
| 3                 | 1         | 3         | 3           | 17.367                 | 241.453                 |
| 4                 | 1         | 4         | 4           | 19.719                 | 266.98                  |
| 5                 | 2(44)     | 1         | 2           | 20.33                  | 287.859                 |
| 6                 | 2         | 2         | 1           | 21.537                 | 271.945                 |
| 7                 | 2         | 3         | 4           | 18.877                 | 258.322                 |
| 8                 | 2         | 4         | 3           | 20.499                 | 268.444                 |
| 9                 | 3(41)     | 1         | 3           | 18.109                 | 253.866                 |
| 10                | 3         | 2         | 4           | 20.951                 | 291.297                 |
| 11                | 3         | 3         | 1           | 21.822                 | 306.193                 |
| 12                | 3         | 4         | 2           | 20.559                 | 303.392                 |
| 13                | 4(38)     | 1         | 4           | 16.198                 | 269.908                 |
| 14                | 4         | 2         | 3           | 20.273                 | 299.572                 |
| 15                | 4         | 3         | 2           | 20.221                 | 305.174                 |
| 16                | 4         | 4         | 1           | 20.747                 | 303.392                 |

The results of the 16 tests were visually compared. As shown in Table 3, the good conditions that can be obtained are: the good condition of the tensile strength index is the No. 11 test, the test condition is A3B3C1, and the good condition of the elongation at break index is Test No. 11, the test condition was A3B3C1. As shown in Table 4, by calculating the range, the test conditions were as follows: a good test condition for the tensile strength index was A3B4C1, and a good test condition for the elongation at break index was A4B4C1.
Table 4. Range analysis of test results.

| Factors            | A         | B         | C         |
|--------------------|-----------|-----------|-----------|
| Tensile strength   | 18.229    | 18.776    | 21.143    |
| K1                 | 20.311    | 19.531    | 19.118    |
| K2                 | 20.36     | 19.572    | 19.062    |
| K3                 | 19.36     | 20.381    | 18.936    |
| K4                 | 2.131     | 1.605     | 2.207     |
| R                  |           |           |           |
| Elongation at Break| 262.826   | 276.687   | 294.161   |
| K1                 | 271.642   | 277.642   | 286.045   |
| K2                 | 288.687   | 277.785   | 265.834   |
| K3                 | 294.512   | 285.552   | 271.627   |
| K4                 | 31.686    | 8.865     | 28.327    |

It can be seen from the magnitude of the range R that the order of significance of each factor to each index is: tensile strength C→A→B, and elongation at break is A→C→B.

Factor A is in the first position for the elongation at break index, and is in the second position for the tensile strength index, while factor C is in the first position for the tensile strength index and the second position for the elongation at break index. While considering the contribution of the mass fraction of A and C to the index, the comprehensive factor C should be selected as 1 level. The factor B is not a significant factor for the tensile strength index and the elongation at break index, and considering the contribution of the mass fraction of the factor B to the index, the comprehensive factor B should be selected as 4 level. Factor A is a significant factor for the tensile strength index and the elongation at break index. Considering the third and fourth levels of the A factor, the tensile strength of the 3 level is 4.91% higher than that of the 4 level, and the elongation at break is 1.98%. It is consistent with the shortest results of vulcanization time and scorch time in Table 1, which further shows that the mechanical properties of NR vulcanizate are the best. Therefore, after comprehensive consideration, the factor A should be selected as 3 levels, and the good test condition after comprehensive balance is A3B4C1.

It can be seen from Figure 2 that the values of true stress and true strain of NR vulcanizate are different under different ratios, which indicates that different ratios have significant effects on the mechanical properties of NR, and the values of true stress and true strain in test No. 11 are the largest, and they are 88.58 MPa, 1.402, with the corresponding mass parts of 41g CB, 3g GE, 1g SiO2; The values of true stress and true strain in test No. 12 are 82.81 MPa and 1.394 respectively after test No. 11 and test No. 16. The corresponding mass fractions are 41 g CB, 4 g GE, 2 g SiO2. When the mass fraction (4g) of the factor GE is fixed, the test factor CB/SiO2 mass fraction of the No. 4 test, the No. 8 test, the No. 12 test and the No. 16 test is gradually smaller, the true stress increases from 72.31MPa to 83.64MPa, and the true strain increases from 1.3 to 1.395. The value shows an increasing trend. This may be the result of the specific surface area of GE, further indicating that 4g GE has a greater effect on NR vulcanizate than CB/SiO2. When the mass fraction (3g) of the factor GE is fixed, the true stress and true strain values first increase and then decrease when the mass fraction of factor CB/SiO2 in test No. 3, No. 7, No. 11 and No. 15 changes. The maximum value appeared in the No. 11 test, which was 88.58 MPa and 1.402 respectively, and the corresponding mass parts were 41 g CB, 3 g GE, and 1 g SiO2. This indicates that the CB/SiO2 ratio of 41/1 has a great influence on the mechanical properties of NR vulcanizate, which is consistent with the maximum values of tensile stress and elongation at break shown in Table 3, which indicates that the mechanical properties of NR vulcanizate are the best. After a comprehensive balance, a good test condition is A3B4C1, and the corresponding mass fraction is 41 g CB, 4 g GE, 1 g SiO2.
Figure 2. The mechanical properties of NR vulcanized rubber were studied under different ratios.

3.3. Microstructure Analysis
In the analysis of vulcanization characteristics and mechanical properties of NR vulcanize, the optimum ratio of CB/GE/SiO₂ was obtained, and the corresponding mass fraction was 41 g CB, 4 g GE, 1 g SiO₂. The microscopic analysis of the cross-section structure of NR vulcanizate helps to further explain that under the optimal ratio of CB/GE/SiO₂, the dispersion state of the filler has a great influence on the mechanical properties of NR vulcanizate. Therefore it is necessary to carry out cross-sectional microstructure analysis of the proportioned NR vulcanizate.

Figure 3. SEM photographs of different proportions of CB/GE/SiO₂. CB/GE/SiO₂ (mass ratio): a—50/0/0; b—38/4/1; c—41/3/1; d—41/4/2

In Figure 3(a), the fracture surface of the NR rubber compound is relatively smooth, in which the white particles are attributed to the unreacted ZnO particles as the active agents in the vulcanization system. The cross-section of the NR rubber compound in (b) and (d) is rough, and the inside is dispersed with a plurality of sheets having a width of 2-8 μm and a thickness of 200-500 nm, which may be a surface-attached rubber-bonded graphene; at the same time, there are some irregular-shaped smaller-sized protrusions which may be a fillers such as CB/SiO₂/ZnO containing a bonding rubber. After
observation, (d) is more uniform than (b), which may be related to the synergistic enhancement of CB/SiO₂. When comparing (c) with (d), the black shading is agglomerated carbon black particles. The carbon black particles are uniformly dispersed in the rubber matrix and the interface is the most blurred. Most of the particles are embedded in the rubber compound, indicating that the materials have strong bonding effect, so the dispersion is the best, so that the tensile strength and elongation at break of the NR vulcanizate are the largest, which is consistent with the results shown in Figure 3. Moreover, in (d) there are some small white spherical aggregates which form agglomerates. The presence of these agglomerates leads to the generation of stress concentration points, as the result, the tensile strength and elongation at break of NR vulcanizate are slightly lower than those of (c) NR vulcanizate, which are the most consistent with the values of tensile stress and elongation at break shown in Table 3, which further indicates that the mechanical properties of the NR vulcanizate are the best. After a comprehensive balance, a good test condition is A3B4C1, and the corresponding mass fraction is 41 g CB, 4 g GE, 1 g SiO₂.

4. Conclusion

a) In the analysis of vulcanization characteristics, when the mass fraction of graphene is 4g, the fraction of CB/SiO₂ gradually decreases, and AM also decreases, which may be due to the tiny diameter size of the particles with a smaller role of physical cross-linking points in the dispersion of rubber molecular chains, which in turn leads to a decrease in the degree of cross-linking of the system. The vulcanization time and scorch time increase first and then decrease, which may be related to the specific surface area of carbon black and white carbon black. The smaller the specific surface area is, the faster the vulcanization rate of the rubber compound, and the shorter the vulcanization time are, thus the mechanical properties of the NR vulcanizate are improved.

b) Design multi-index orthogonal test and calculate the size of the range R by calculation. The order of significance of each factor to each index is: tensile strength is C→A→B, and elongation at break is A→C→B. The good test condition for the tensile strength index is A3B4C1, and the good test condition for the elongation at break index is A4B4C1. Among the calculated values of true stress and true strain, the value under the condition of A3B3C1 is the largest, a good test condition after comprehensive balance is A3B4C1, and the mass fraction of the factors are 41g CB, 4g GE, 1g SiO₂, the maximum true strain in the corresponding mechanical properties is 139.8%, and the maximum true stress is 85.695MPa.

c) The results of cross-sectional morphology analysis show that when the mass fraction of CB/GE/SiO₂ is 41/3/1, the dispersion of the filler is best in the NR matrix, and the mass fraction of CB/GE/SiO₂ is 41/4. The results of /2-degree cross-sectional morphology analysis show that the mechanical properties of NR vulcanizate are very good. The best ratio after final equilibrium is consistent with the results obtained by orthogonal test, which is 41g CB, 4g GE, 1g SiO₂.

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