Influence of Carbon Black on Aging Properties of Natural Rubber

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Abstract. The influence of carbon black on the aging properties of NR was studied by adding different grades and contents of carbon black. The results show that the hardness, tensile strength and tear strength of NR increased with the increase of carbon black level and content, while the elongation at break and Akron abrasion decreased. After hot air accelerated aging and ultraviolet aging, the tensile strength, elongation at break and Akron abrasion of NR decreased, the tear strength first decreased and then increased, and the shore hardness gradually increased. With the increase of carbon black grade and quantity, the change rate of natural rubber aging properties, such as shore hardness, tensile strength, elongation at break, tear strength and Akron abrasion, became smaller and smaller.

1. Introduction

Since the beginning of rubber industry, natural rubber is the material with the best balance of various properties in elastomer, and also the general rubber with the best application. Natural rubber is a kind of isoprene polymer. Its chemical name is cis-1,4-polyisoprene and molecular structure is [1]

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The specific gravity of natural rubber is between 0.91 and 0.93, and the glass transition temperature is between -70°C and -72°C [2]. There are many unsaturated double bonds in natural rubber, so it has poor aging resistance. The rubber products made of only natural rubber are lack of good mechanical properties and have low use value. Carbon black is the best and most used reinforcing agent in rubber industry, which can greatly improve the performance of natural rubber [3]. Zhao Zhizheng’s research showed that carbon black could improve the tensile strength, tear strength and wear resistance of natural rubber. S. Borros studied that carbon black could strongly react with the vulcanizate of natural...
rubber and improve the structure of natural rubber vulcanizate [4]. Zhang Xinhui’s research showed that carbon black could significantly improve the conductivity of natural rubber [5]. In this paper, the influences of carbon black on the natural rubber aging properties were studied by adding different grades and contents of carbon black.

2. Test materials and methods

2.1. Test materials
Natural Rubber (NR), Yunnan Agricultural Reclamation Yun Oak Investment Co., Ltd; Zinc Oxide, Shanghai Mogao New Materials Co., Ltd; Stearic Acid, Jinan Aoxing Chemical Co., Ltd; Carbon Black N330, N660, Zhengzhou Juli Chemical Co., Ltd; Promoter TMTD, Products of Shanghai Chengjin Chemical Co., Ltd. The others were all commercial industrial products. The rubber formula was shown in Table 1.

| Component       | 1#  | 2#       | 3#       |
|-----------------|-----|----------|----------|
| Natural Rubber  | 100 | 100      | 100      |
| Zinc oxide      | 2   | 2        | 2        |
| Silicon dioxide | 6   | 6        | 6        |
| Sulfur          | 1   | 1        | 1        |
| Carbon black    | 30(N660) | 15(N330) + 15(N660) | 30(N330) |
| Stearic acid    | 0.8 | 0.8      | 0.8      |
| Promoter TMTD   | 1   | 1        | 1        |

2.2. Test methods and equipments
The natural rubber was plasticized in YZM-2L mixer, then stearic acid, zinc oxide, silicon dioxide was added to mix, and carbon black was added to mix finally. The vulcanizing agent was added to the XK-160 twin-roll mill starter, and the mixture was uniform, then the lower tablet was made. The samples were cured on YJ-450 plate vulcanizer after 24 hours. Vulcanization parameters were 145℃ × 20 min, 10 MPa. The properties of vulcanized specimens were tested after being parked for 48 hours.

1) Tensile properties and tear strength were tested by ETM computer controlled electronic universal testing machine. Tensile properties were tested according to GB/T528-2009, and the tensile speed was 500 mm/min.

2) The tearing strength was tested according to GB/T529-2008 by the right-angled specimens. The tearing speed was 500 mm/min, and the testing temperature was (23±2)℃.

3) The hardness was tested by Shore A rubber hardness tester according to GB/T531.1-2008.

4) The abrasion resistance of rubber was tested by MH-1689 clone machine and operated according to GB1689-2014.

5) Jw-8001 type ozone aging test chamber produced by Shanghai Juwei instrument and Equipment Co.; Ltd. is used for 47℃ hot air thermal aging test according to GB/t3512-2014.

6) The h-zw-p ultraviolet accelerated weathering test chamber produced by Shanghai Boyi Experimental Equipment Co.; Ltd. was used for the test according to GB / t16585-1996. The test conditions were: irradiance 0.49w/m², 70℃, 8h; condensate 50℃, 4H; 125 cycles.
3. Test results and analysis

3.1. Infrared spectrum of natural rubber

![Fig. 1 IR results of natural rubber](image)

It can be seen from Figure 1 that there is a methyl vibration peak at 2924.10 cm\(^{-1}\), C = C bond stretching vibration peak near 1709.11 cm\(^{-1}\), and a cis structure peak at 840.07 cm\(^{-1}\), all of which are characteristic peaks of natural rubber, indicating that the material is natural rubber.

3.2. Physical properties of natural rubber

From Table 2 and Figure 2 we can find that with the decrease of carbon black level and quantity, rubber hardness, tensile strength and tear strength gradually increase, and elongation at break and Akron abrasion gradually decrease. This is because with the decrease of carbon black level, the particle size of carbon black gradually decreases and the specific surface area increases [6]. The number of active sites on the surface of carbon black increased, the entanglement of rubber macromolecular chain increased, the crosslinking density increased and the crosslinking bond increased [7]. As a result, hardness and strength increase, elongation at break and Akron wear decrease.

| Test items         | 1#   | 2#   | 3#   |
|--------------------|------|------|------|
| Shore A hardness   | 61.5 | 66.5 | 76   |
| Tensile strength /MPa | 21.2 | 23.8 | 27.4 |
| Elongation /%      | 538  | 499  | 478  |
| Tear strength /kN/m | 19.8 | 24.7 | 29.6 |
| Akron wear/1.61km/cm\(^3\) | 0.252 | 0.226 | 0.189 |

![Fig. 2 Effect of different carbon black grades and contents on physical properties of natural rubber](image)
3.3. Physical properties of natural rubber after hot air aging

After 47℃, 96%RH hot air accelerated aging and heat resistance test, the change of physical properties of rubber is shown in Table 3 and figure 3. With the increase of aging time, the tensile strength, elongation at break and Akron wear decreased, the tear strength first decreased and then increased, the shore hardness gradually increased, and the change trend slowed down with the increase of aging time. With the increase of carbon black grade and quantity, the changes of shore hardness, tensile strength, elongation at break, tear strength and Akron abrasion of rubber are smaller and smaller. This is due to the fact that with the extension of aging time, the rubber surface becomes dense, the cross-linking produced in the aging process is too much, the rubber surface strength is improved, and the uneven defects of pores and bumps are produced on the rubber surface, resulting in the decrease of rubber strength and elongation at break, and the increase of shore hardness [8].

Table 3 Physical properties of rubber after hot air aging

| Test items            | Time/h | 1#  | 2#  | 3#  |
|-----------------------|--------|-----|-----|-----|
| Shore A hardness      |        |     |     |     |
|                       | 500    | 63  | 68  | 78  |
|                       | 1000   | 65  | 69.5| 79.5|
|                       | 1500   | 65.5| 70  | 80  |
| Tensile strength /MPa |        |     |     |     |
|                       | 500    | 19.5| 22.2| 26.3|
|                       | 1000   | 18.5| 21.4| 25.6|
|                       | 1500   | 17.9| 20.9| 24.9|
| Elongation/%          |        |     |     |     |
|                       | 500    | 475 | 450 | 436 |
|                       | 1000   | 442 | 428 | 418 |
|                       | 1500   | 427 | 413 | 404 |
| Tear strength /kN/m   |        |     |     |     |
|                       | 500    | 12.9| 18.7| 24.7|
|                       | 1000   | 13.7| 19.9| 25.9|
|                       | 1500   | 14.2| 20.6| 26.4|
| Akron wear/1.61km/cm³ |        |     |     |     |
|                       | 500    | 0.231| 0.202| 0.169|
|                       | 1000   | 0.203| 0.185| 0.152|
|                       | 1500   | 0.2  | 0.184| 0.15 |

Fig. 3 Change diagram of physical properties of natural rubber after hot air aging

3.4. Physical properties of natural rubber after ultraviolet aging

After irradiance of 0.49w/m², 70℃, 8h; condensate of 50℃, 4H; 125 cycles of ultraviolet aging test, the change of physical properties of rubber is shown in Table 4 and Figure 4. With the increase of UV aging time, the tensile strength, elongation at break and Akron wear decreased, the tear strength first decreased and then increased, the shore hardness gradually increased, and the change trend slowed down with the increase of aging time. With the increase of carbon black grade and quantity, the changes of shore hardness, tensile strength, elongation at break, tear strength and Akron abrasion of
rubber are smaller and smaller. After the same aging time, the tensile strength, elongation at break and Akron abrasion of UV aging are less than those of hot air aging. Both the shore hardness and tear strength are greater than the hardness after hot air aging. This is because the temperature of ultraviolet aging is 70 ℃, while the temperature of hot air aging is 47 ℃, which is an important factor affecting the aging performance of rubber. With the increase of temperature, the internal crosslinking of rubber increases, so that the rubber surface becomes more compact, and there are more pores and uneven defects on the rubber surface, resulting in the decrease of rubber strength and elongation at break, and the increase of shore hardness.

Table. 4 Physical properties of rubber after ultraviolet aging

| Test items       | Time/h | 1# | 2# | 3# |
|------------------|--------|----|----|----|
| Shore A hardness |        |    |    |    |
| 500              | 66     | 71.5| 80.5|
| 1000             | 67.5   | 72.5| 82 |
| 1500             | 68.5   | 73  | 83 |
| Tensile strength /MPa |        |    |    |    |
| 500              | 18.2   | 19.7| 23.6|
| 1000             | 16.4   | 17.5| 22.1|
| 1500             | 16.1   | 16.8| 21.8|
| Elongation /%    |        |    |    |    |
| 500              | 453    | 438 | 421|
| 1000             | 436    | 418 | 406|
| 1500             | 429    | 409 | 398|
| Tear strength /kN/m |     |    |    |    |
| 500              | 13.5   | 19.5| 25.1|
| 1000             | 14.6   | 20.5| 26.5|
| 1500             | 14.9   | 21.2| 27.3|
| Akron wear/1.61km/cm3 |   |    |    |
| 500              | 0.226  | 0.195| 0.164|
| 1000             | 0.212  | 0.187| 0.157|
| 1500             | 0.208  | 0.182| 0.152|

Fig. 4 Change diagram of physical properties of natural rubber after ultraviolet aging

4. Conclusions
1) With the increase of carbon black grade and content, the hardness, tensile strength and tear strength of NR increased gradually, while the elongation at break and Akron abrasion decreased gradually.

2) After hot air aging and UV aging tests, the tensile strength, elongation at break and Akron abrasion of natural rubber gradually decreased, the tear strength first decreased and then increased, and the shore hardness gradually increased.

3) With the increase of carbon black grade and quantity, the change of shore hardness, tensile strength, elongation at break, tear strength and Akron abrasion of NR is smaller and smaller.

Acknowledgments
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