Effect of the Purple carbon black on the properties of NR/BR blend

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Abstract. Purple black is light colored mineral filler mining in recent years in Hainan. The effect of the dosage of the purple carbon black and purple carbon black modificated by Si69 on the vulcanization characteristics, mechanical properties, thermal stability, the damping performance of NR/BR blend rubber were studied, and the blending adhesive tensile sections were analyzed by SEM. Research showed that, with the increasing dosage of the purple carbon black, vulcanization characteristics of NR/BR blend had a little change. Adding the purple carbon black into blending had a reinforcing effect. when the dosage of the purple carbon black was 20, the mechanical properties of blending adhesive was good; Coupling agent Si69 had a modification effect on the purple carbon black. With increasing dosage of Si69, performance of the rubber was improved initially and then decreased; when the mass fraction of Si69 was 8% of the dosage of the purple carbon black, rubber performance was optimal. Purple carbon black had no obvious effect on thermal stability of the rubber, but it improved the damping rubber temperature and damping factor.

Keywords:natural rubber ;BR; purple carbon black; mechanical properties

1. Introduction

Natural rubber (NR) has excellent elasticity, viscoelasticity, the comprehensive mechanical properties and processability, good cold resistance and electrical insulation, but the heat resistance and weather resistance is poor. The modified NR and other analysing blending are used to improve the damping performance [1]. Butadiene rubber (BR) is a crystalline rubber without self-reinforcing effect; it has low elasticity and high strength, good low temperature resistance, wear resistance, small heat generating, and it’s commonly used to manufacture tire tread [2].

Purple carbon black is a kind of light color mineral filler recently developed in Hainan [3]. Report about the application of the purple carbon black in rubber products has not been found within China or

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abroad. Based on NR, BR as raw materials, this paper studied the effect of the dosage of the purple carbon black and the effect of Si69-modified purple carbon black on the vulcanization characteristics, mechanical properties, thermal stability, the damping performance of NR/BR blend rubber, in order to provide the reference for further study of its application in rubber products.

2. Experimental

2.1 Materials

Natural rubber (NR), SCR - 5, Bayi rubber factory in Hainan; Butadiene rubber (BR9000), China petroleum and chemical co., LTD., Beijing yanshan branch; Green purple carbon black (PCB, chemical components are shown in table 1), 1500 mesh, Hainan long sheng mining co., LTD; Stearic acid, zinc oxide, accelerator M, promoting agent, accelerator NOBS, antiager D antiager 264, antiager 2246, naphthenic oil, sulfur, Si69 (Bis-(3-thiethoxy silylpropyl)-tetrasulfide) were commonly used in rubber industry.

Table 1 The chemical composition of the purple carbon black

| Content        | Mass    |
|----------------|---------|
| SiO_2          | >55%    |
| Al_2O_3        | >18%    |
| Fe_2O_3        | <7.5%   |
| K_2O           | <5%     |
| TiO_2          | >0.5%   |
| pH             | 5.8±0.2 |
| Calcinations of weightlessness | <6.5% |
| Oil absorption/10g | 2~3.5 |
| The content of water | <1.0% |

Note: The chemical composition analysis according to GB/T4734-1996

2.2 Preparation of compounds

Natural rubber was masticated on a laboratory two-rollmill (JTC - 752 type) and reclaimed rubber was added at different percentages. The blends were prepared as per the formulation given in the below according to the following sequence: NR, BR - stearic acid - zinc oxide-accelerator M - accelerator D - accelerator NOBS - Antiager 264 - filler - naphthenic oil, sulfur, Si69 (Bis-(3-thiethoxy silylpropyl)-tetrasulfide) to get the rubber compound. The formulations: NR. 80; BR 20; Stearic acid 1.5; Zinc oxide 5; promoter M 0.6;

Accelerator D 0.3; Accelerator NOBS 1; Antiager 264 0.8; Naphthenic oil 5; Sulfur 2.2; Purple carbon black variables.

2.3 Characterization of reclaimed rubber

Thermal gravimetric analyzer was used to conduct vulcanized rubber thermal analysis. With nitrogen as the carrier gas, and a heating rate of 10℃ /min, each sample, weighing about 10 ~ 15mg, was heated from 25 ℃ to 600 ℃. records were obtained as TG curves and DTG curves (mettler Toledo company)

2.4 Rheology

Rheology of compounds was analyzed using rubber processing analyzer

(RPA) (Prescott co., LTD) with strain sweep test at 145 ℃ and 117 Hz (cycle per minute) frequency.
2.5 Curing
Cure rate, scorch time (t_{10}) and cure time (t_{90}) of the rubber compounds were detected with an oscillating disk curemeter at a test temperature of 145 °C. The compounds were compression molded using a 25 tone press (Huzhou star rubber machinery company) at 145°C based on their respective t90 value.

2.6 Mechanical properties
Tensile properties were measured following GB/T528-1998 and GB/T528-91 using a microcomputer control electronic tensometer (Shanghai hualong test instrument co., LTD) at 500mm/min cross head speed. Hardness tests (shore A) were conducted using LX-A (Jiangsu) hardness tester according to GB/ T531-1999. Abrasion loss tests were conducted using WX-76 (Wuxi) resilience and abrasion testers according to GB/T 1689-1998. Fatigue life of vulcanizates was measured using a fatigue to failure tester (401A, Shanghai) at 100°C for 24 hours according to GB 3512-2001.

2.7 Morphology
The failure mechanisms of rubber vulcanizates were investigated using an scanning electron microscope (SEM), (S-3000N, Japan) at 25kv accelerating voltage, examining fractured surfaces of rubber vulcanizates obtained after pulling off.

2.8 Dynamic Mechanical Analyzer (DMA)
Test conditions: stretching mode, the temperature ranges from -100 °C to 100 °C, heating rate of 10°C / min, test frequency is 5Hz.

| Table 2 The effect of purple carbon black content on the properties of NR/BR blends |
|----------------------------------|----------|----------|----------|----------|----------|
| Properties               | Consumption / mass parts | 0      | 10      | 20      | 30      | 40      |
| M (N/m)                  | M (N/m)   | 0.974   | 1.094   | 1.109   | 1.169   | 1.185   |
| M (N/m)                  | M (N/m)   | 0.105   | 0.075   | 0.075   | 0.080   | 0.080   |
| t_{10}/min               | t_{10}/min | 2.35    | 2.17    | 2.55    | 2.33    | 2.27    |
| t_{90}/min               | t_{90}/min | 6.07    | 5.88    | 5.45    | 5.57    | 5.42    |
| Shore A hardness / Shore A |          | 42      | 45      | 46      | 47      | 45      |
| Tensile strength /MPa     | Tensile strength /MPa | 9.29    | 10.99   | 15.56   | 14.23   | 13.68   |
| 300% Modulus /MPa         | 300% Modulus /MPa   | 1.32    | 1.9     | 2.31    | 2.77    | 2.84    |
| Elongation at break /%    | Elongation at break /% | 750    | 670    | 740    | 650    | 660    |
| Tensile set at break /%   | Tensile set at break /% | 12      | 12     | 16     | 20     | 20     |
| Tear strength / (kN/m)    | Tear strength / (kN/m) | 19.68   | 27.43   | 26.06   | 25.86   | 25.20   |
| Abrasion loss /%          | Abrasion loss /%    | 1.05    | 1.27    | 1.61    | 1.95    | 2.39    |

3. Results and discussion
3.1 Mechanical properties of NR/BR vulcanizates filled with the purple carbon black
The mechanical properties of NR/BR vulcanizates were presented in Table 2. From table 2, the addition of the purple carbon black in NR/BR blend slightly lower M, improved M and changed little on t_{10} and t_{90}. Namely, the vulcanization characteristics of rubber had no obvious impacts. Purple carbon black had a certain reinforcing effect on NR/BR blends. This may be due to the surface active
group of purple carbon black particle that can combine with rubber reinforcing effect (not quite understand this sentence). With the increasing amount of carbon black, the hardness and tear strength changed little; but the tensile strength and the elongation at break increased initially and then decreased. The 300% Modulus increased. The quality change of the abrasion increased gradually. When the mass fraction of purple carbon black was 20%, the blends had good performance.

3.2 Mechanical properties of NR/BR vulcanizates filled with the purple carbon black modified by coupling agent Si69

The affect of different dosage of Si69 modified purple carbon black on the properties of NR/BR blend vulcanizates was analyzed. The result was shown in table 3.

According to Table 3, with the increasing mass fraction of coupling agent Si69, NR/BR blend of $M_H$ was slightly lower, $M_L$ became slightly higher and $t_{90}$ and $t_{10}$ went down slightly. This demonstrated that the amount of coupling agent Si69 had no obvious impacts on vulcanization characteristics of NR/BR vulcanizates. The modified purple carbon black could further improve the performance of NR/BR vulcanizates. this is due to the findings that, Si69 transformed to silanol by hydrolyzing which combined with the surface of purple carbon black, and the organic functional group of Si69 reacted with the double bonds of the rubber molecular chain, resulting in a bridge linking up the purple carbon black molecules and rubber molecules, thereby enhancing the effect of purple carbon black. With the increase of the mass fraction of coupling agent Si69, Shore A hardness basically remained unchanged; The tensile strength increased initially and then decreased. The tear strength showed a trend of increase; the change percentage of abrasion loss was slightly lower, which showed that the wear resistance had improved. 8% of NR/BR blends that containing 20 phr purple carbon black, which was modified by the mass fraction of coupling agent Si69, exhibited desirable mechanical properties. When the dosage of the coupling agent increased, the reinforcing effect of the purple carbon black on NR/BR blend weakened. This indicated that the coupling agent Si69 may act as diluents which can weaken the interaction between the purple carbon black molecules and the rubber molecules. [5, 6]

| Properties          | 0  | 4  | 6  | 8  | 10 |
|--------------------|----|----|----|----|----|
| $M_H$ (N/m)        | 1.109 | 0.949 | 1.00 | 1.03 | 0.939 |
| $M_L$ (N/m)        | 0.075 | 0.075 | 0.095 | 0.1 | 0.095 |
| $t_{10}$/min       | 2.55 | 2.12 | 2.05 | 1.98 | 1.88 |
| $t_{90}$/min       | 5.45 | 5.03 | 5.08 | 5.12 | 5.32 |
| Shore A hardness / Shore A | 46   | 48   | 48   | 47   | 48   |
| Tensile strength /MPa | 15.56 | 16.72 | 17.60 | 18.02 | 16.02 |
| 300% Modulus /MPa  | 2.31 | 2.70 | 2.84 | 3.10 | 3.02 |
| Elongation at break /% | 740  | 650  | 660  | 670  | 630  |
| Tensile set at break /% | 16   | 16   | 12   | 16   | 16   |
| Tear strength / (kN/m) | 25.06 | 26.56 | 27.66 | 27.80 | 30.58 |
| Abrasion loss /%   | 1.61 | 1.61 | 1.71 | 1.43 | 1.54 |

3.3 Thermal degradation

General thermal stability referred to the thermal stability of the polymer chain, namely the main chain of polymer molecular chain after heated the fracture, the decomposition of side chain, oxidation and structured process. [7] The experiment was conducted under nitrogen atmosphere, with a 10 °C / min temperature programmed rate. The thermal stabilities of different dosage of filling were determined, and the TG and DTG curve were shown in Fig. 1.
Fig.1 showed that NR/BR vulcanizates of weightlessness was divided into two stages: the first stage was the quickest stage for weightlessness with the temperature range of 300 °C ~ 450 °C. The NR and BR thermal decomposition of the backbone of the polymer happened in the first stage. The second stage was carbonization process, and the weightlessness curve flattens.

From Fig.1, the initial decomposition temperatures of three kinds of filling system were all about 350 °C. The final degradation temperature was at 440 °C, which demonstrated that the purple carbon black had certain effects on the thermal stability of the vulcanizates.

![Fig. 1 The TG and DTG analysis of different filling system](image)

Note: 1.0 per the purple carbon black 2.20 per the purple carbon black 3. 20 per the purple carbon black modified by 8% Si69

3.4 SEM studies

Fig.2 showed the SEM photographs of fractured surface of NR/BR vulcanizates. Comparing Fig.2 (a), (b) and (c) showed that the section of NR/BR vulcanizates without purple carbon black was smooth, and showing obvious homogeneous structure. While the blend section of added purple carbon black displayed obvious two phase structure, The particles in 2 (c) were uniform, and the surface showed deep hole. This indicated that the modified purple carbon black had improved the compatibility of NR/BR. This finding has also been demonstrated in the previous mechanical property analysis.

![Fig.2 The cross-section of SEM](image)

3.5 Damping properties of NR/BR vulcanizates

When the filler packaged into the rubber matrix, the filler particles could affect the network of the
polymer matrix, which also affect the dynamic performance of a filled vulcanizates[8]. The dynamic mechanics performance of the purple carbon black filled vulcanizates was shown in figure 3. According to the graph, the damping factor of vulcanizates increased, the glass transition temperature of vulcanizates filled with modified purple carbon black was higher, and the damping factor was bigger after the purple carbon black was added.

Fig. 3 The DMA curve of vulcanizates
1. without purple carbon black 2. 20 per of the purple carbon black 3. 20 per of the purple carbon black modified by 8% Si69

Conclusion
Addition of the purple carbon black had little effect on the vulcanization characteristics of NR/BR vulcanizates, but the addition could increase mechanical properties of the vulcanizates. When the dosage of the purple carbon black was 20, the mechanical properties of the vulcanizates were better. With the increasing dosage of the purple carbon black, abrasion loss increased gradually. When the Si69 mass fraction was 8%, the modification effect of the purple carbon black was optimal. The TG and DTG analysis showed that the purple carbon black had no effect on the thermal stability of vulcanizates. The damping factor of the modified purple carbon black filled NR/BR vulcanizates was higher than the unmodified ones, and the effective damping temperature increased.

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