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Use of Insoluble Sulfur Crystex Cure Pro in Belt Compound of Passenger Car Tires

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Abstract: The application of insoluble sulfur Crystex Cure Pro in the belt compound of passenger car tires was investigated. The results showed that, after insoluble sulfur Crystal Cure Pro replaces insoluble sulfur HD OT 20 for the belt compound of passenger car tires, the mixing time of the compound was shortened, the Mooney scorch time was prolonged, and the high thermal stability and dispersion of insoluble sulfur were improved.

Key words: insoluble sulfur; passenger car tire; belt compound; high thermal stability; dispersion

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In order to ensure that vulcanized rubber meets specific performance requirements, great amounts of sulfur (greater than 2 percent) must be added in the formula design. The solubility of common sulfur in natural rubber (NR) at room temperature is about 1.5 percent. When the amount of sulfur used exceeds the solubility limit, sulfur migrates to the surface of the rubber and recrystallizes, forming micro-crystals on the surface of finished compound. This is known as sulfur bloom; bloom interferes with inter-ply adhesion primarily due to reduced tack. Bloom events in factories can be very costly causing significant wastes of energy and materials [1-2].

In the belt compound, sulfur plays a crucial role in ensuring the property of adhesion between steel cords and the rubber. Sulfur loading levels in these compounds invariably exceeds solubility limits thereby necessitating the use of insoluble sulfur. At room temperature, insoluble sulfur neither generates bloom nor migrates in rubber. Therefore, in the formula the amount of sulfur used can be increased to promote the adhesion between steel cords and the rubber, thus ensuring the adhesion performance of the steel cord fabric. Insoluble sulfur is an accepted and preferred curing agent for steel-wire rubber [3-4].

Insoluble sulfur is polymeric sulfur, a common allotrope of sulfur [3]. Sulfur (S_8, cyclooctasulfur,) undergoes ring-opening polymerization (ROP) at a high temperature (160℃) converting into long chains of sulfur. Quenched at a low temperature, the polymeric sulfur crystallizes becoming the insoluble sulfur product used today for commercial purposes. However, as a material in a “metastable” state, insoluble sulfur is easily reverted to common sulfur under high temperature or basic condition [5]. Besides being influenced by external factors, the stability is subject more to the internal structure of the insoluble sulfur including its crystal form and crystallization level. Failing to dissolve in rubber, the insoluble sulfur can be difficult to disperse

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in the rubber compound, which directly affects the use performance of the steel cord rubber. Therefore, high thermal stability and dispersion of insoluble sulfur become two properties which receive wide attention.

Crystex Cure Pro is a new-generation, commercialized insoluble sulfur product developed by Eastman Chemical (China) Co., Ltd. With a mass fraction of total sulfur of 0.90, Crystex Cure Pro offers better thermal stability and dispersion and faster powder incorporation capacity compared to the last generation of insoluble sulfur HD OT 20, so it can shorten the mixing time of the rubber material and improve production efficiency.

From the perspectives of high thermal stability and dispersion, we studied the application of insoluble sulfur Crystex Cure Pro in the belt compound of passenger car tires.

1 Experiment

1.1 Materials

NR, brand number BJ-4, produced in Thailand; carbon black, N375, Shandong Best Chemical Technology Co., Ltd.; white carbon black, 1165MP, Rhodia White Carbon Black (Qingdao) Co., Ltd.; insoluble sulfur, Crystex Cure Pro and HD OT 20, Eastman Chemical (China) Co., Ltd.

1.2 Formula

Reference formula: NR, 100 portions; carbon black N375, 52 phr; white carbon black, 10 phr; zinc oxide, 8 phr; antiager 4020, 2 phr; B-20-S resin, 1 phr; adhesive RA-65, 4 phr; insoluble sulfur HD OT 20, 5 phr; accelerator TBBS, 1.3 phr.

In the experiment formula, 4.44 phr of insoluble sulfur Crystex Cure Pro replaced 5 phr of insoluble sulfur HD OT 20. For other material proportions, see the above reference formula.

1.3 Equipment and Instruments

GK255N and GK400 internal mixers, produced by Yiyang Rubber & Plastics Machinery Group Co., Ltd.; S-type four-roller calender, made by Comerio Ercole of Italy; FLIR A655SC infrared camera for temperature test, made by FLIR Systems Inc.; PREMIER Mooney viscometer (MV) and PREMIER MDR curemeter, made by Alpha Pro Tech, Inc.; 5967-type universal tensile machine, made by Instron Limited; and CP116388 optical microscope, made by Keyence Corporation of Japan.

1.4 Mixing Technology

The rubber materials are mixed using three mixing processes in three steps. Mixing at step 1 and step 2 was performed in the GK400 internal mixer, with the rotor speed being 45 $r•min^{-1}$ for both steps. The step 1 mixing process was: raw rubber, carbon black, zinc oxide, stearic acid, antiager, etc., → press the ram (45 s) → lift the ram → press the ram (45 s) → lift the ram → press the ram (40 s) → lift the ram → discharge the rubber (150°C); the step 2 mixing process was: the rubber from step 1 mixing → press the ram (40 s) → lift the ram → press the ram (45s) → lift the ram → press the ram (40 s)→ lift the ram → discharge the rubber (150°C); the step 3 mixing was performed in the GK255N internal mixer, with the rotor speed being 25 $r•min^{-1}$. The mixing process was: the rubber from step 2 mixing, insoluble sulfur, and accelerator → press the ram (30 s) → lift the ram → press the ram (30 s) → lift the ram → discharge the rubber (110°C).

To reduce the influence of the mixing processes on the experiment results, we used the same mixing process to carry out the mixing successively for 10 batches of the compound with the reference formula, 10 batches of the compound with the experiment formula, and 10 batches of the compound with the reference formula, respectively.

1.5 Property Testing

Each property was tested according to relevant national standards.

2 Results and Discussion

2.1 Physical and Chemical Analysis

Table 1 shows the results of the physical and chemical analysis of two types of insoluble sulfur.

According to Table 1, compared with insoluble sulfur HD OT 20, insoluble sulfur Crystex Cure Pro increased in the mass fraction of effective sulfur but decreased in the mass fraction of oil, and after it was heated at 105°C for 15 minutes, Crystex Cure Pro increased in the mass fraction of insoluble sulfur.

Table 1 Result of the physical and chemical analysis of two types of insoluble sulfur

Item	Crystex Cure Pro	HD OT 20
Mass fraction of total sulfur × 10^2	89.60	79.50
Mass fraction of insoluble sulfur × 10^2	87.05	75.80
Mass fraction of oil ×10^2	10.40	20.50
Acidity/%	0.010	0.003
Mass fraction of ash content × 10^2	0.01	0.03
Mass loss on heating (80°C)/%	0.35	0.14
Mass fraction of sieve residue with a particle diameter of 75 μm × 10^2	0.10	0.10
Mass fraction of insoluble sulfur heated at 105°C for 15 minutes × 10^2	87.50	81.20

2.2 Mixing Process

The rubber discharge temperature in the mixing process was set to reach the mixing temperature. In the experiment, as the rubber discharge temperature was reached, the mixing time of the compound with the experiment formula was shortened by 25 s from 165 s to 140 s compared with that of the compound with the reference formula. This is possibly resulted from the fact that insoluble sulfur HD OT 20 is spherical, whereas insoluble sulfur Crystex Cure Pro has irregular shapes, which better helps its dispersion.

To comprehensively understand the temperature distribution of the compounds, we tested the rubber discharge temperature of each batch of the mixed rubber with an infrared camera to measure the temperature. The camera device shot the rubber discharge video of each batch of the compounds for about 20 s. In the shooting process, the device generated infrared images of 50 frames per second, with each video containing N temperature test images, each pixel point of the image per frame denoted a temperature collection point, namely, each temperature test image had M temperature test points. We first took the maximum value from M temperature test points per image and calculated the average value of all these maximum values, with the maximum value and average value being respectively denoted by *Mmax* and *Mavg*. Each video (for each batch of the compound) contained N M_{max} values and M_{avg} values, and the average values of *Mmax* and *Mavg* were then calculated, respectively, which were recorded as $N_{avg}(M_{max})$, $N_{max}(M_{max})$, $N_{avg}(M_{avg})$ and $N_{max}(M_{avg})$. Finally, we calculated the average values of four types of temperature for 10 batches of the compound involved in each experimental scheme. Table 2 shows the test result of the mixed rubber discharge temperature.

Table 2 Measurement results of the mixed rubber discharge temperature ℃

Item	First 10 batches of the compound with the reference formula	10 batches of the compound with the experimental formula	Last 10 batches of the compound with the reference formula
$N_{avg}(M_{max})$	123.4	124.7	124.0
$N_{max}(M_{max})$	129.5	129.5	130.0
$N_{avg}(M_{avg})$	94.8	95.8	97.5
$N_{max}(M_{avg})$	97.2	98.0	100.9

According to Table 2, the rubber discharge temperature slightly rose as the mixing process progressed. This is due to the mode of rubber discharge at a controlled temperature. It follows that there is not much difference in rubber discharge temperature between the compound with the experimental formula per batch and the compound with the reference formula.

2.3 Calendering Process

We first calendered 10 batches of the compound with the experimental formula, and then 20 batches of the compound with the reference formula. We tested the stacked rubber between No. 2 roller and No. 3 roller of the steel cord fabric calender with an infrared temperature test method. The test method was the same as that used for the mixing process. Table 3 shows the test result.

Table 3 Result of the temperature test on the stacked rubber in the calendering process ℃

Item	The compound with the experimental formula	The compound with the reference formula
$N_{avg}(M_{max})$	109.4	112.4
$N_{max}(M_{max})$	114.3	117.5
$N_{avg}(M_{avg})$	90.6	91.2
$N_{max}(M_{avg})$	92.3	92.9

According to Table 3, compared with the compound with the reference formula, the compound with the experimental formula slightly decreased in temperature in the calendering process but the difference in temperature was not much, which indicates that the mixing process performance of the compounds was not greatly influenced when insoluble sulfur Crystex Cure Pro replaced insoluble sulfur HD OT 20.

2.4 Vulcanization Property

Table 4 shows the vulcanization properties of the compounds.

Table 4 Vulcanization properties of the compounds

Item	The compound with the experimental	The compound with the reference formula

	formula	
Mooney viscosity [ML(1 + 4)100℃]	81	81
Mooney scorch time t_s(135℃)/min	18.13	16.63
Vulcanometer data (151℃)		
F_L/(dN•m)	3.19	3.24
F_{max}/(dN•m)	28.82	28.71
t_{10}/min	5.28	5.29
t_{90}/min	18.38	18.68

According to Table 4, compared with the compound with the reference formula, the compound with the experimental formula had the same Mooney viscosity but longer Mooney scorch time, and they were similar in other properties, which indicates that when insoluble sulfur Crystex Cure Pro is used in place of insoluble sulfur HD OT 20, Mooney scorch time can be prolonged, and that the material processing safety can be improved while similar Mooney viscosity and vulcanization speed are ensured.

2.5 Thermal Stability

We measured the soluble sulfur content of the pre-calendering mixing rubber and the post-calendering mixing rubber for steel cord fabric application. The difference between the two can indicate the thermal stability of insoluble sulfur in the mixed rubber. The test result is shown in Table 5.

According to Table 5, under the same calendering process conditions, compared with the compound with the reference formula, the pre-calendering rubber compound with the experimental formula has its mass fraction of soluble sulfur decrease by 24%; the mass fraction of soluble sulfur in the post-calendering rubber for steel cord fabric application decrease by 51%; compared with the pre-calendering rubber compound with the experimental formula, the post-calendering rubber compound has its mass fraction of soluble sulfur increase by 63%; compared with the pre-calendering compound with the reference formula, the post-calendering compound has its mass fraction of soluble sulfur increase by 152%. This indicates that in the mixing and calendering processes of the compounds, insoluble sulfur Crystex Cure Pro is lower in conversion rate and better in thermal stability.

Table 5 Mass fractions of soluble sulfur in the pre-calendering and post-calendering rubber compounds

Item	Experimental formula	Reference formula
Pre-calendering mixing rubber	0.0019	0.0025
Post-calendering rubber for steel cord fabric application	0.0031	0.0063
Difference between the pre-calendering and post-calender compounds	0.0012	0.0038

2.6 Dispersion

Dispersion of insoluble sulfur in rubber was indicated by two test methods: testing the tensile strength of the vulcanized rubber and its adhesion to steel cords; testing the size and uniformity of the dispersed sulfur particles in the mixing rubber by using an optical microscope to observe the mixed rubber compounds.

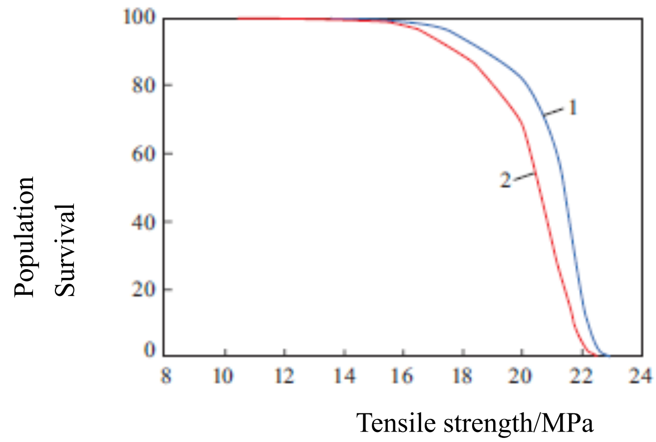
In the process of vulcanization and temperature rise, insoluble sulfur gradually converted into soluble sulfur which evenly diffused to the surrounding. Large sulfur particles took longer time to convert and diffuse. The rubber network had completed the cross-linking reaction before these sulfur particles diffused fully and evenly. Therefore, the sulfur concentration sites excessively cross-linked, and the excessively cross-linking areas became the focal points of stress in the stress process, which finally resulted in reduced tensile strength of the vulcanized rubber.

Based on the testing of numerous samples, the curves made from the survival populations of tensile strength (which refers to the fraction of samples which reached a certain tensile strength value to the total samples) could reflect the dispersion of sulfur in the compounds. Higher vulcanizing temperature could give full play to the dispersion indicated by this principle, and the vulcanizing condition of tensile test samples was 170℃ × (t_{90} + 1 min). Likewise, the test result of the adhesion between the vulcanized rubber and steel cords could also reflect the dispersion of insoluble sulfur in the compounds. The vulcanizing condition of the adhesion test samples was 151℃ × (t_{90} + 6min).

2.6.1 Effective rate curve of tensile strength

To maintain the dispersion of insoluble sulfur in the mixing rubber, we used the unrolled raw rubber for vulcanization of tensile strength test samples. We selected 10 batches of the compound with the experimental formula and 10 batches of the compound with the reference formula. Each batch of the compound had 8 vulcanized samples, each of which was trimmed into 5 dumbbell-shaped test pieces. Thus, we took 400 samples respectively to make the effective population survival curves based on the tensile strength test result of the samples. The test result is shown in Figure 1.

According to Figure 1, at the same tensile strength, the compound with the experimental formula had a greater population survival than that with the reference formula. This indicates that the compound with the experimental formula is higher in tensile strength than that with the reference formula, and that the dispersion of insoluble sulfur Crystex Cure Pro in the compounds is significantly improved.

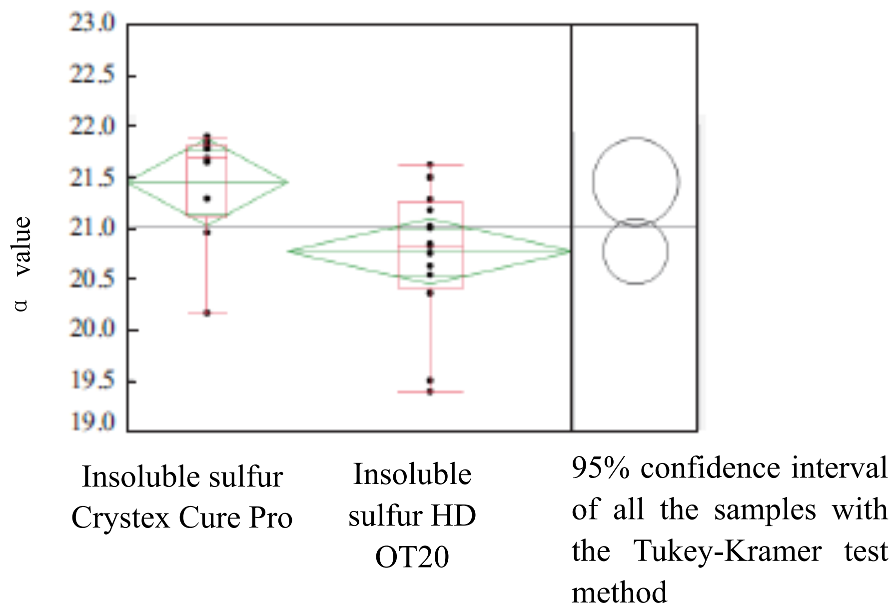


1 - experimental formula; 2 - reference formula

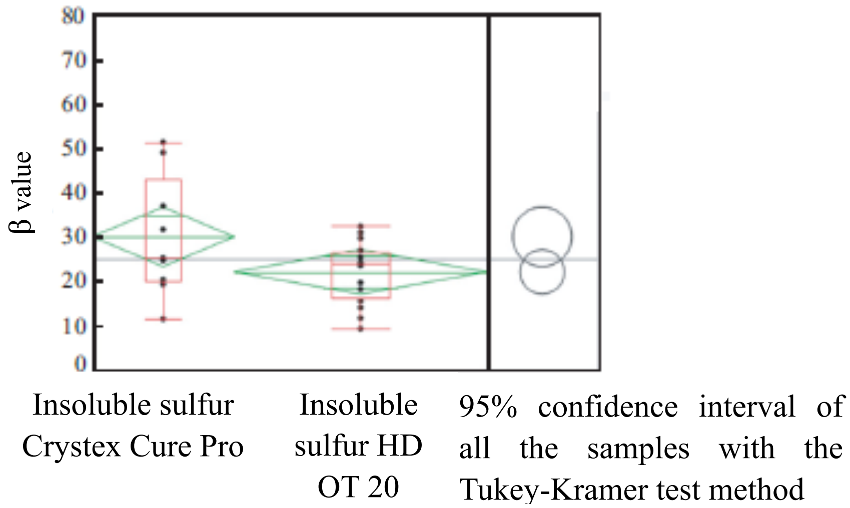
Figure 1 Population survival curves of tensile strength of the compounds

Alpha, α, value is defined as the tensile strength at the survival of 1/3 of the population of samples, and beta, β, value as the gradient of Weibull distribution curve (log calculation twice). The greater α value and β value, the better dispersion of insoluble sulfur. We took α value and β value from the population survival curve of the tensile strength of each batch of the compound to make a statistical analysis. The result is shown in Figure 2.

According to Figure 2, when the confidence interval was 95%, the compound with the experimental formula had significantly greater α value and β value than that with the reference formula. This indicates that insoluble sulfur Crystex Cure Pro in the compounds is better in dispersion.



(a) α value



(b) β value

Figure 2 Statistical result of α value and β value on the population survival curves of the compounds

The result of the discrete statistical analysis of the obtained tensile strength data is shown in Figure 3.

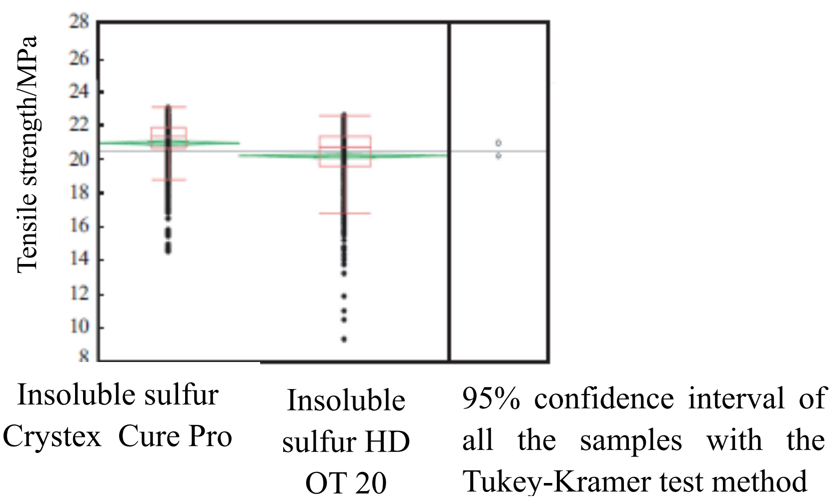


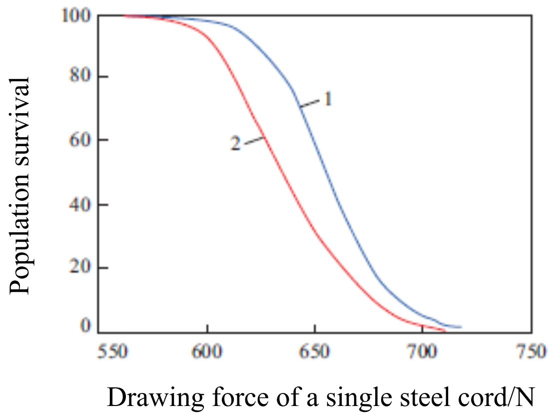
Figure 3 Discrete statistical result of the tensile strength of the compounds

According to Figure 3, when the confidence interval was 95%, the compound with the experimental formula had significantly greater tensile strength than that with the reference formula.

2.6.2 Population survival curve of the withdrawal force of a single steel cord

We tested the property of the adhesion between the compounds and steel cords by conducting a withdrawing force test of a single steel cord. In each test, samples were taken from

10 batches of the compound, with 39 samples from each batch of the compound for a total of 390 data points. We plotted the population survival (which refers to the fraction of samples reaching a certain drawing force value to total samples) curves based on the withdrawing force test values of a single cord. The result is shown in Figure 4.



Note: same as Figure 1

Figure 4 Population survival curve of the drawing force of a single wire

According to Figure 4, under the condition of the same withdrawing force of a single steel cord, the compound with the experimental formula had a significantly greater population survival than that with the reference formula, indicating that the adhesion property of the compound with the experimental formula is notably improved.

The result of the discrete statistical analysis on the obtained withdrawing force data of a single steel cord is shown in Figure 5.

According to Figure 5, when the confidence interval was 95%, the compound with the experimental formula had significantly higher than that with the reference formula in terms of the withdrawing force of a single steel cord.

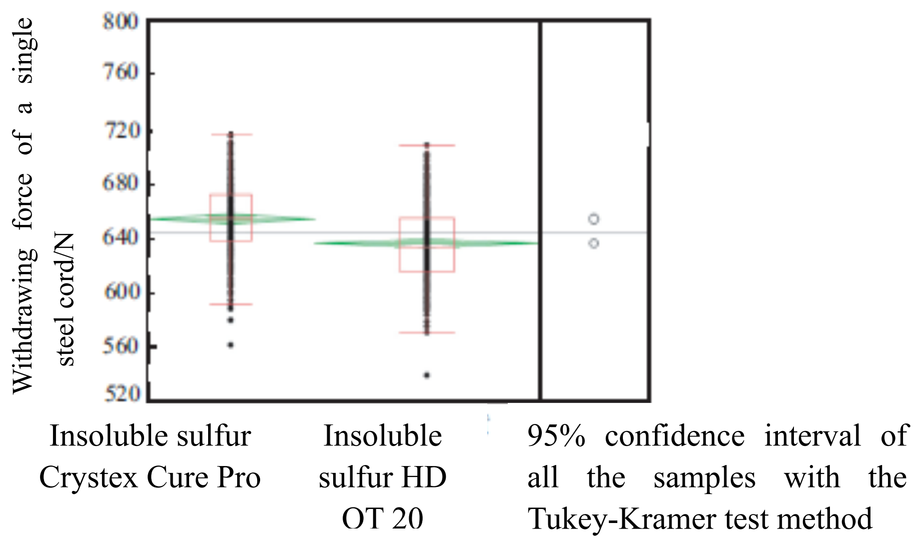
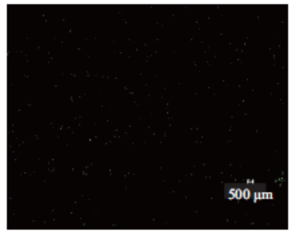


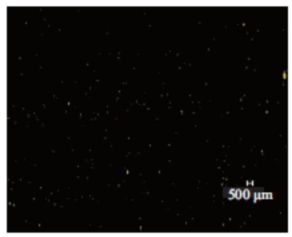
Figure 5 Discrete statistical result of the withdrawing force of a single steel cord

2.6.3 Statistical analysis of the quantity of sulfur particles in the mixing rubber

Using an optical microscope, we observed the sections of the compound with the experimental formula and of that with the reference formula. The sample size is 50 mm x 20 mm. The observation result is shown in Figure 6.



(a) The compound with the experimental formula

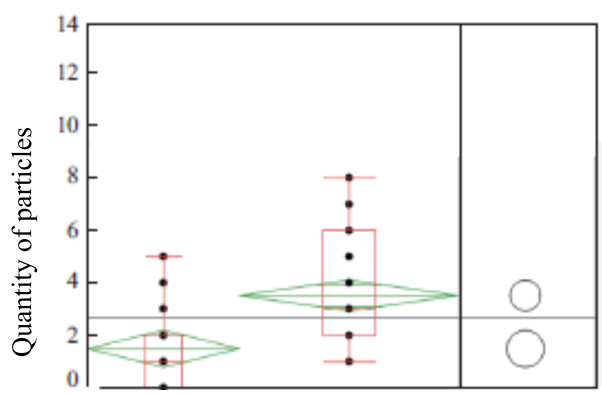


(b) The compound with the reference formula

Figure 6 Section pattern of the compounds (the sections were amplified by 30 times)

According to Figure 6, compared with the compound with the reference formula, the compound with the experimental formula significantly decreased in the quantity of large sulfur particles, with the particles becoming smaller and uniformly distributed.

We made statistics of the quantity of those sulfur particles with a diameter of over 200 µm. Figure 7 shows the statistical result.



Insoluble sulfur Crystex Cure Pro

Insoluble sulfur HD OT 20

95% confidence interval of all the samples with the Tukey-Kramer test method

Figure 7 Analysis of the quantity of sulfur particles with a diameter of over 200 µm

According to Figure 7, compared with the compound with the reference formula, the compound with the experimental formula significantly decreased in the quantity of sulfur particles with a diameter of over 200 μm, indicating that insoluble sulfur Crystex Cure Pro is better than insoluble sulfur HD OT 20 in terms of dispersion in the rubber compounds. Figure 8 shows the analysis result of the quantity of sulfur particles per unit area.

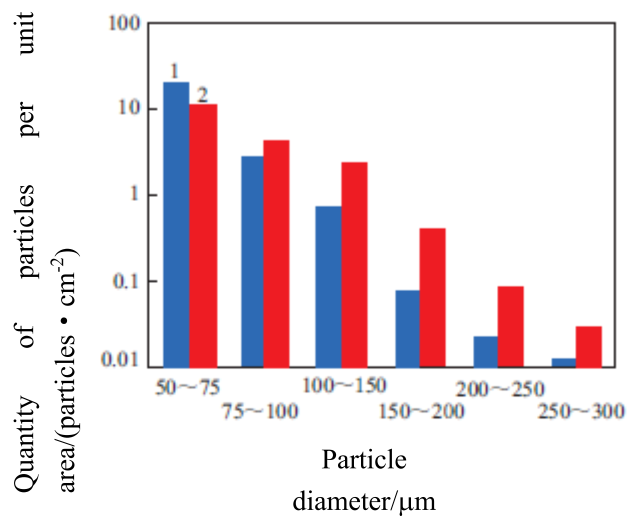


Figure 8 Statistics of the quantity of sulfur particles with a diameter of over 200 μm per unit area

According to Figure 8, compared the compound with the reference formula, the compound with the experimental formula saw a greater proportion of sulfur particles with a diameter of 50 to 75 μm, gradually decreased proportions of the particles with a diameter of over 75 μm, and a significantly decreased proportion of the particles with a diameter of over 200 μm. This indicates that insoluble sulfur Crystex Cure Pro is better than insoluble sulfur HD OT 20 in terms of dispersion in the compounds.

3 Conclusion

(1) After insoluble sulfur Crystex Cure Pro replaces insoluble sulfur HD OT 20 in the belt compound of passenger car tires, the mixing time of the compounds is shortened, their Mooney scorch time extended, and their processing safety improved.

(2) In the mixing and calendering processes of the compounds, insoluble sulfur Crystex Cure Pro is lower in conversion rate and better in thermal stability than insoluble sulfur Crystex HD OT 20.

(3) According to the population survival curve of tensile strength of vulcanized rubber, the population survival curve of the withdrawing force of a single steel cord, and the observation of the microscope, insoluble sulfur Crystex Cure Pro is significantly better than insoluble sulfur HD OT 20 in terms of dispersion in the compounds.

References:

[1] Yong Zhanfu, Gao Yang, He Yousheng et al. The "Coordination and Control of Melting and Decomposition of Insoluble Sulfur in the Compound Mixing Process" [J] *China Rubber Industry*, 2018,65(12):1349-1354.

[2] Wang Yanqiu. *Basis of Rubber Materials* [M]. Beijing: Chemical Industry Press, 2006.

[3] Wang Jiaming. The "Current Production and Supply Situation and Market Prospects of Insoluble Sulfur" [J]. *Fine Chemical Industrial Raw Materials & Intermediates*, 2010(4):18-21.

[4] Li Peng, Wang Shudong, Lin Ke et al. The "Application of Insoluble Sulfur Crystex Cure in Steel-bonded Compound" [J]. *Tire Industry*, 2018,38(10):612-616.

[5] Hu Weiqing, Huang Wanli, Wu Libao et al. The "Application Properties of Insoluble Sulfur" [J]. *Contemporary Chemical Industry*, 2015,44(3):473-476.

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