Formulation Design of Deep Watertight Connector

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Abstract. In order to make the watertight connector localized, this paper mainly studies the outer insulating material neoprene 2442 (CR2442) of the watertight connector from the material, and improves the physical and mechanical properties of the CR2442 and the adhesion of the CR2442 to the brass by designing the formula. The performance and finalization of the watertight connector molding and vulcanization molds are designed to meet the molding needs of watertight connectors. Through research, it is found that the CR2442 optimized by this paper has good physical and mechanical properties and adhesive properties.

1. Introduction
From the 1940s to around 1960 and after more than 20 years of development, the watertight connectors gradually extended from the original simple plug-in type to the inductive coupling with complex connections; although the connection of watertight connectors has been huge change, but the watertight connector has not yet achieved a breakthrough in structural engineering [1-3]. The research on underwater connectors in developed countries has gradually matured after nearly 80 years of development. The general working depth can reach 6,000 meters, and the maximum working depth can exceed 10,000 meters [4]. At present, foreign famous manufacturers of watertight connectors include subcon and seacon. Foreign watertight connectors have the advantages of large depth of dive, stable energy and signal transmission, long working time, etc., and are favored by many countries.

Most of the watertight connectors used in the domestic marine environment are imported from abroad, which is not only expensive but also has a long period of periodicity, which greatly limits China’s research on marine science and the exploration of marine resources [5]. In comparison, China’s research on watertight connectors started late. The current research level and the results obtained are only equivalent to the initial stage of research in developed countries, and there is still a big gap compared with developed countries. The stability of watertight connectors is not good. About half of the watertight connectors developed in China are prone to failure during energy and signal transmission. The failure of the watertight connector will cause unrestricted loss [6-10].

2. Experiment
Firstly, the equipment required for the preparation of the compounding compound has an internal mixer and an open mill. The mixing process is: first, the initial temperature of the internal mixer is set. The temperature in one zone is 70 °C, and the temperature in the second zone is 70 °C, the temperature in
the three zones is: 70 °C. Secondly, the internal mixer speed is set. The internal mixer speed is 70 r/min. When the temperature of each zone reaches 70 °C, the neoprene rubber 2442 is mixed. The mixing process is: (1) the CR2442 and small materials were simultaneously added to the mixer for 1 min; (2) carbon black N550 was added and kneaded for 1 min; (3) white carbon black and V700 aromatic oil were sequentially added to the internal mixer and kneaded for 1 min; (4) Pay close attention to the change of the temperature of the rubber compound. When the temperature is between 100 °C and 110 °C, the glue is discharged after 60-90 s. After the glue is discharged, the mixing compound is quickly placed on the open mill for 1 or 2 times. The purpose is to quickly cool the compounded rubber to prevent the scorching phenomenon of the rubber compound. After the roller is cooled, the rubber is weighed. It is used to judge whether there is any leakage during the mixing process. After the rubber compound is cooled (generally cooled for 2 to 3 hours), the rubber compound is placed on the open mill to be opened, and the roll distance is adjusted to be small when the rubber is opened. After the glue is accumulated on the mill, the accelerator DM, zinc oxide and ordinary sulfur are sequentially added. After the rubber compound rotates for 5 to 6 weeks with the roller, the rubber is cut 5 times on the left and right. After the accelerator DM, zinc oxide and ordinary sulfur are mixed uniformly, the roller is appropriately adjusted to make the triangle bag and the round bag 5 times. Mix well and then pass through 8 to 10 times, then press and cool for use. The cooling time is generally 12 h.

3. Result Analysis

3.1. Effect of Vulcanization System on Physical Properties of Neoprene

Figure 1 shows the effect of vulcanization system on the tear strength, tensile strength, Sauer hardness and water absorption of chloroprene rubber. It can be seen from the comparison of samples 1, 2 and 3 that the content of vulcanized rubber is reduced with the decrease of zinc oxide content. The breaking strength showed a downward trend. By comparison of 3 and 4, it was found that the breaking strength gradually decreased with the decrease of magnesium oxide content. The tear strength does not change substantially with the decrease of ordinary sulfur content, and the tear strength tends to increase with the decrease of the DM content of the vulcanization accelerator. The main reason is that zinc oxide is the main vulcanizing agent of chloroprene rubber 2442. Magnesium oxide is used as a scorch inhibitor of chloroprene rubber 2442 to prevent scorching phenomenon during vulcanization of the rubber compound. When the content of magnesium oxide is low, the vulcanized rubber will be scorched. If the rubber is scorched during the vulcanization process, the tearing strength of the vulcanized rubber will be lowered. The sulfur content does not substantially affect the neoprene rubber. The reason is that the neoprene rubber is a polar rubber and is difficult to react with sulfur. The vulcanization accelerator DM can accelerate the vulcanization rate of the rubber. If the vulcanization rate is too fast under the same vulcanization time, it will lead to excessive sulfur, which leads to the breakage of the molecular chain, thereby reducing the tear strength of the vulcanize. The effect of various substances in the vulcanization system on the tear strength of vulcanized rubber is shown in figure 1. As the content of zinc oxide decreases, the tear strength of vulcanized rubber exhibits a downward trend. The main reason is that on the one hand, the decrease of zinc oxide content causes the occurrence of under-sulphur phenomenon, resulting in the relatively low density of the crosslinked grid, which leads to the decrease of the tear strength of the vulcanized rubber compound. On the other hand, the sulfur content decreases with the sulfur content. The probability of vulcanization with the rubber becomes large, and the sulfur and the rubber compound form a lower crosslink bond, resulting in a decrease in tear strength. It can be seen from the comparison of the samples 3, 4, 5, and 6 that the tear strength of the vulcanized rubber increases with the decrease of the DM content of the magnesium oxide, the ordinary sulfur, and the vulcanization accelerator. The main reason is that on the one hand, the reduction of sulfur content is beneficial to the participation of zinc oxide in the vulcanization of the rubber compound. On the other hand, the decrease of the vulcanization rate due to the decrease of the
DM content makes the probability of sulfur production of the rubber compound become smaller, which leads to the tearing of the vulcanized rubber compound. The crack strength increases. Through experiments, it can be seen that changing the influence of each substance in the vulcanization system on the Sauer hardness of the vulcanized rubber compound is small (table 1). Under the premise of ensuring the physical and mechanical properties of the vulcanized rubber compound, the vulcanization can be adjusted by changing the proportion of other materials in the formulation.

| Table 1. Ratio of each material of the vulcanization system. |
|-------------------------------------------------------------|
| Vulcanization system | 1 | 2 | 3 | 4 | 5 | 6 |
| ZnO               | 8 | 6 | 4 | 4 | 4 | 4 |
| MgO               | 4 | 4 | 4 | 2 | 2 | 2 |
| S                 | 4 | 4 | 4 | 4 | 2 | 2 |
| DM                | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.15 |

Figure 1. Effect of vulcanization system on physical properties of neoprene.

The absorption of moisture by the compound reduces the service life of the watertight connector and the efficiency of signal and energy transfer. Therefore, exploring the water absorption properties of the materials in the formulation is an important factor in ensuring the service life, signal and energy transmission efficiency of the watertight connector. Through the study of the water absorption of the above samples, it was found that the water absorption rate of the other vulcanized rubber materials except for the sample 1 was relatively low, and the stability of the watertight connector under water operation was largely reduced. By studying the effect of the vulcanization system on the properties of the neoprene rubber, we can see that the sample 4 has a large breaking strength and tensile strength, and also has a low water absorption rate, so next we will zinc oxide: magnesium oxide: sulfur: DM = 4: 2: 4: 0.3 as a basic formula to study the effect of the reinforcing system on the physical properties of chloroprene rubber.

3.2. Effect of Reinforcing System on Physical and Mechanical Properties of Neoprene

In this paper, carbon black N550 and white carbon black are used to reinforce the neoprene. The following table 2 shows the specific ratio of the reinforcing system and the test results of physical properties.

The design idea of Formulation 1 to 5 is to add Carbon Black N550 to Formulation 2 based on Formulation 1, to increase the content of white carbon black on the basis of Formulation 2 to obtain Formulation 3, and to add Carbon Black N550 on the basis of Formulation 3. The content was obtained in Formulation 4, and the content of white carbon black was added on the basis of Formulation 4 to obtain Formulation 5, which formed a pairwise comparison. When formula 1 and
formula 2 are compared and found to be 10 parts of silica, the tensile stress of the vulcanized rubber increases with the increase of carbon black N550 content. The main reason is that carbon black N550 has a good reinforcing effect. When the white carbon black is 10 parts, it will not affect the dispersion degree of carbon black N550 in the rubber compound. Therefore, as the carbon black N550 content increases, the modulus of the vulcanized rubber compound shows an upward trend. It was found that when the carbon black N550 was 20 parts, the shrinkage stress of the vulcanized rubber showed a decreasing trend with the increase of the content of white carbon black. The main reason was that the white carbon black had a rate of vulcanization. The effect, when the white carbon black increases, can reduce the rate of the vulcanization reaction, resulting in the occurrence of sulfur vulcanization of the vulcanized rubber compound. Therefore, when the carbon black N550 is 20 parts, the vulcanization compound is fixed with the increase of the white carbon black content. The stress is reduced. Comparing equation 3 with equation 4, it is found that when the content of white carbon black is 15 parts, the modulus of vulcanize increases with the increase of carbon black N550 content. The main reason is that carbon black N550 has good reinforcing effect, when the white carbon black is 15 parts, it will not affect the dispersion degree of carbon black N550 in the vulcanized rubber compound. Therefore, as the carbon black N550 content increases, the modulus of the vulcanized rubber compound shows an upward trend. Compared with formula 5 and formula 5, it is found that the shrinkage stress of vulcanized rubber exhibits a decreasing trend with the increase of white carbon black content. The main reason is: on the one hand, when the carbon black N550 is 30 parts, the content of white carbon black will affect the dispersion of the small material in the compounding compound, resulting in uneven mixing of the rubber compound, thereby causing a decrease in the modulus of the vulcanized rubber compound. On the other hand, when the content of white carbon black is increased, the rate of the vulcanization reaction is lowered to cause insufficient vulcanization at a specific vulcanization time, thereby causing a decrease in the modulus of vulcanization of the vulcanize.

| Formula          | 1    | 2    | 3    | 4    | 5    |
|------------------|------|------|------|------|------|
| N550             | 10   | 20   | 20   | 30   | 30   |
| White carbon black| 10   | 10   | 15   | 15   | 20   |
| V700             | 10   | 10   | 10   | 10   | 14   |
| 100% Fixed stress| 2.13 | 2.29 | 2.08 | 4.16 | 3.44 |
| 200% Fixed stress| 7.63 | 10.55| 7.68 | 9.90 | 7.73 |
| 300% Fixed stress| 10.07| 13.26| 13.17| 15.26| 12.64|
| Fixed stress     | 20.69| 24.54| 21.35| 23.34| 20.82|
| Sauer hardness   | 57   | 61   | 60   | 64   | 65   |
| Mooney viscosity | 38.62| 40.25| 48.65| 57.49| 50.44|
| Tc10             | 4.08 | 4.36 | 4.52 | 6.14 | 4.21 |

It can also be seen from table 2 that when the total number of carbon black N550 and white carbon black increases. In the experiment of bonding neoprene to brass, Mooney viscosity is an important parameter affecting the bonding effect, so the Mooney viscosity is as small as possible under the premise of ensuring the comprehensive performance of the vulcanized rubber compound. When N550: silica = 30: 15, Mooney viscosity value: 57.49, is conducive to injection molding of watertight connectors. Through experimental studies we have used this ratio as an investigation of the effect of the bonding system on the properties of neoprene and brass bonding.

3.3. Effect of Bonding System on the Bonding Properties of Neoprene and Brass

The effect of the bonding system on the tear strength of the rubber compound is shown in figure 2. As the total number of parts of the bonding system increases, the tearing strength of the vulcanized rubber material basically shows a downward trend, and the main reason is that the bonding system mainly
plays a role. Adhesion, when the content of the bonding system increases, the percentage content of the rubber compound and carbon black N550 in the overall formulation is reduced, thereby affecting the tear strength of the vulcanized rubber compound, and a part of the material in the adhesive system is involved in the rubber compound. The vulcanization reaction produces a sulfide having a lower bond energy, resulting in a decrease in the tear strength of the vulcanizate. From the comparison between Formulation 2 and Formulation 4 and Formulation 6 and Formulation 8, it can be seen that the total number of binders in the formulation is equal, but the tear strength of the vulcanized rubber compound is quite different, mainly due to RA. Although -65 is mainly based on bonding, it can combine a certain number of rubber molecular chains to increase the number of meshes of vulcanized rubber compounds, resulting in a strong increase in the tearing of vulcanized rubber compounds. When SL-3022: RA-65: Cobalt cobaltate is 1: 5: 0.9, the 100% modulus is the largest, and the overall trend of the larger tensile stress is in the formula with more RA-65 content (table 3). RA-65 can better combine with the molecular chain of CR2442 to form a mesh structure with a certain strength. The increase of the number of meshes will increase the modulus of the vulcanizate. However, when the content of RA-5 is high, the tensile stress will also decrease to a certain extent. The reason for this phenomenon is that the SL-3022 in the formulation and the physical and mechanical properties of cobalt sulphate on the rubber compound will be It has a certain influence, so it will lead to a decrease in the tensile stress. The constant tensile stress indicates the force required to produce a certain deformation of the vulcanized rubber. During the insertion and removal of the watertight connector, the neoprene will undergo a certain tensile deformation, so the tensile stress of the vulcanized rubber is as large as possible.

Table 3. The orthogonal test of the bonding system.

|       | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  |
|-------|----|----|----|----|----|----|----|----|----|
| SL-3022 | 1  | 1  | 1  | 3  | 3  | 3  | 5  | 5  | 5  |
| RA-65  | 1  | 3  | 5  | 1  | 3  | 5  | 1  | 3  | 5  |
| White carbon black | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| Cobalt cobaltate | 0.3 | 0.6 | 0.9 | 0.6 | 0.9 | 0.3 | 0.9 | 0.3 | 0.6 |

Figure 2. Effect of bonding system on properties of neoprene.

During the vulcanization of the rubber compound, SL-3022 and RA-65 form a bonding resin in the vulcanized environment of the rubber compound, and the SL-3022 and the RA-65 are sticky. The resin can participate in the vulcanization of the rubber compound and the adhesion of the rubber compound to the brass. The cobalt ruthenate catalyzes the adhesion between the brass and the sulfur to promote the chemical reaction between the brass and the sulfur. The effect of the copper sulphide bonding layer, the chemical reaction equation of vulcanization and bonding is as follows:

Vulcanization reaction:
When the content of cobalt cobalt is too high, it will easily lead to the conversion of cuprous sulfide to copper sulfide. Because copper sulfide is a metal sulfide with low bond strength, excessive copper sulfide will reduce the extraction force of copper wire and affect the neoprene. It can be seen from figure 2 that the change of the content of each substance in the adhesive system has a great influence on the adhesive force, and the adhesion of the samples 1 to 9 first increases and then decreases, when SL-3022: RA-65: sodium acid Cobalt is the most adhesive at 3: 1: 0.6. The adhesion at the left end of this content tends to increase, because SL-3022 is a resorcinol donor and RA-65 is a methylene donor. When the content of SL-3022 and RA-65 increases at the right end of this content, the extraction force of copper wire gradually decreases. The main reason is that the Mooney viscosity of the rubber compound greatly affects the fluidity of the rubber compound. This leads to a decrease in adhesion. On the other hand, when the SL-3022 and RA-65 increase, the adhesion reaction rate increases. Since the time taken for vulcanization of the rubber is fixed, the extension of the remaining time after completion of the adhesion reaction will make the conversion of more cuprous sulfide to copper sulfide with lower bond energy eventually leads to a decrease in adhesion.

We was found to have the best adhesion effect, and its formulation was: CR2442, 100; N550, 30; white carbon black, 15; V700, 10; SAD, 0.5; MgO, 2; Si-3022, 3, RD, 1; 4010, 2; CO20, 0.6; ZnO, 4; S, 2; DM, 0.15; RA-65, 1.

4. Conclusion
The increase or decrease of the content of zinc oxide, magnesium oxide, common sulfur and vulcanization accelerator DM in the vulcanization system has little effect on the positive vulcanization time Tc90, and the vulcanization curve is not significantly flat when the rubber compound is tested without rotor period. In the vulcanization system, the content of zinc oxide, magnesium oxide, ordinary sulfur and vulcanization accelerator DM is gradually decreased. The tear strength, tensile strength and tear strength of the vulcanized rubber are first decreased and then increased. When zinc oxide: oxidation Magnesium: Ordinary sulfur: vulcanization accelerator DM=4: 2: 2: 0.15, the physical and mechanical properties of the vulcanizate are maximized. The increase or decrease of the content of zinc oxide, magnesium oxide, common sulfur and vulcanization accelerator DM in the vulcanization system has little effect on the Sauer hardness of the vulcanized rubber. Under the premise of ensuring the physical and mechanical properties of the vulcanized rubber compound, other adjustments can be made. The content of the material is used to change the Sauer hardness of the vulcanizate. When the content of magnesium oxide is 2 parts, the comprehensive physical and mechanical properties of the vulcanizate are the best, and when the content is more than two, the water absorption rate tends to increase gradually. It is more suitable when the magnesium oxide is 2 parts. The effect of carbon black on the tensile strength and tear strength of the vulcanized rubber in the reinforcing system should not only consider the influence of white carbon black on the dispersion of small materials in the formulation, but also the effect of white carbon black on the vulcanization rate. When carbon black N550: white carbon black = 30: 15, Te10 is the largest, and the processing safety of the rubber is the best. The tensile strength, breaking strength, Mooney viscosity and Te10, the final formula for the bonding of neoprene to brass is: CR2442, 100; N550, 30; silica, 15; magnesium oxide , 2; zinc oxide, 4; ordinary sulfur, 2; V700 aromatic oil, 14; active agent SAD, 0.5; antioxidant RD, 1; antioxidant 4010, 2; accelerator DM, 0.15. SL-3022: RA-65: When the cobalt sulphate = 1: 3: 0.6, the Mooney viscosity is the smallest, the value is: 32.11; the Sauer hardness of the vulcanizate increases with the content of the methylene donor RA-65 The increase, so that the methylene donor RA-65 has the greatest influence on the hardness of the vulcanizate. Through
experimental research, the formula with the largest extraction force is: CR2442, 100; N550, 30; white carbon black, 15; V700, 10; SAD, 0.5; MgO, 2; Si-3022, 3; RD, 1; 4010, 2; CO20, 0.6; ZnO, 4; S, 2; DM, 0.15; RA-65, 1. The extraction force before corrosion is 387.4N, and the extraction force after water corrosion resistance can reach 287.4N. For Formulation CR2442, 100; N550, 30; Silica, 15; V700, 10; SAD, 0.5; MgO, 2; Si-3022, 3; RD, 1; 4010, 2; CO20, 0.6; ZnO, 4; S, 2; DM, 0.15; RA-65, 1, when the vulcanization time is 60 min, the overall physical and mechanical properties of the vulcanizate are the best.

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