Study on Increasing Vulcanization Rate of Ethylene-propylene Rubber

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Abstract. The effects of several commonly used ultra on the vulcanization properties of EPDM vulcanized with sulfur and the vulcanization properties and physical properties of EPDM vulcanized with peroxide were studied. The results showed that BZ and lseg-4 vulcanization rate was fast and frost spraying was not easy. Peroxide tx29-40 can be used to vulcanize EPDM. The activation energy and vulcanization speed of tx29-40 are higher than DCP/TAIC and double 2,5 which can be used for high temperature and rapid vulcanization of peroxide in EPDM.

1. Instruction
In the present domestic and international environment, the rubber industry is very competitive, people are seeking to reduce the cost of the products and to improve their production’s performance, at the same time. How to improve the product all kinds of physical and mechanical properties, and reduce the product cost, improve efficiency must be the most concerned topic of so much manufacturers.

2. Experiment
2.1 The Raw Material
EPDM, brand 4570, made by Dupont USA.; Lseg-4, produced by Guangzhou Jinchangsheng technology co, LTD. Other additives are industrial grade products.

The basic formula of sulfur is EPDM 100. Zinc oxide 5; Stearic acid 2; Promoter M 0.8; Promoter TT 0.2; Paraffin wax 1; Semi-reinforced carbon black 70; Paraffin oil 30; Sulfur 1;The promoter is the variable.

The basic formula of peroxide vulcanization is EPDM 100; Zinc oxide 5; Paraffin wax 1; Semi-reinforced carbon black 70; Paraffin oil 30; Curing agent and crosslinking agent are the variables

2.2 Experimental Equipment
Opening mill S(X)K-160A, Qingdao chemical machinery plant; Vulcanization tester GT-M2000-A, produced by GOTECH Testing Machines Inc; Electronic tension machine ai-7000s, produced by GOTECH Testing Machines Inc; Shore A hardness tester, Shanghai chemical machinery repair plant 4; Electronic balance gt-xb, made by GOTECH Testing Machines Inc.320M

2.3 Sample Preparation
Rubber mixing sequence as follows: EPDM even package roll, rubber additives (promoter, zinc oxide, stearic acid and stabilizer) to carbon black, packing, softener, curing agent, Thin pass technology 6 times until completion of loading the piece, parking sulfide samples for 24 h, vulcanization temperature is 165°C.
2.4 Test
All physical properties are tested according to the corresponding national standards.

3. Results and Discussion

3.1 Selection of Ethylene-propylene Rubber
EPDM includes binary rubber and ternary rubber. The third monomer used in EPDM is non-conjugated diolefins, and its type and dosage have direct influence on vulcanization speed and physical and mechanical properties. [1-3] The characteristics of the three third monomers currently used in industry are shown in table 1. When sulfur vulcanization system is adopted, ENB-EPDM has the fastest vulcanization speed, followed by 1, 4-hd-epdm, and DCPD-EPDM has the slowest vulcanization speed. When using peroxide as vulcanization agent, DCPD-EPDM is the fastest, followed by ENB-EPDM, and 1, 4-HD-EPDM is the slowest. In terms of heat resistance, ENB-EPDM is superior to DCPD-EPDM in terms of 1, 4-HD-EPDM, while in terms of ozone aging resistance, DCPD-EPDM is superior to ENB-EPDM and 1, 4-HD-EPDM. [3-6]

| Name and structure       | Features                                               | Branched |
|--------------------------|--------------------------------------------------------|----------|
| Ethylnorbornene (ENB)    | Fast curing speed; Vulcanizates have high tensile strength; Vulcanizates have little permanent deformation. | A small amount of |
| 1, 4-hexadiene (1, 4-hd) | Vulcanizates compression deformation is small; Medium curing speed, not easy to scorch. | There is no |
| Dicyclopentadiene (DCPD) | The cost is low; Slow vulcanization rate Vulcanizates; Little permanent deformation; Have a bad smell. | high     |

3.2 Vulcanization System

3.2.1 Sulfur System. Sulfur vulcanization system has the advantages in safe operation, moderate vulcanization speed, good comprehensive physical mechanical properties and good co-vulcanization with diolefins rubber, and is the most widely used ternary ethylene propylene rubber vulcanization system.

To keep rubber from frost spraying, the amount of accelerator, also must be lower than its saturated solubility in EPDM. Many accelerators in the lower concentration will occur frosting, so the dosage should not be too high. Often used with a variety of promoters, which can improve the vulcanization speed, and can improve the physical and mechanical properties of vulcanized rubber, and is not easy to spray frost.

The scientific name of accelerator BZ is zinc dibutyl dithiocarbamate, which is an over speed accelerator of natural rubber and synthetic rubber. The vulcanization characteristic data when the dosage of promoter BZ is 0.0.5, 1 and 1.5, respectively, are shown in table 2.

The Table 2 shows that with the increase of the accelerator dosage of BZ, EPDM rubber vulcanization scorch time, is shortened which is bad for the operation safety of rubber. And the vulcanization time is also shortened, which is beneficial to improve the production efficiency of
rubber products, and that means the BZ has obvious promoting effect and high solubility in the ethylene-propylene rubber, so the material will not easy to bloom.

### Table 2. Effect of accelerator BZ on vulcanization characteristics of EPDM

| BZ dosage | 0   | 0.5 | 1.0 | 1.5 |
|-----------|-----|-----|-----|-----|
| Ts1/min   | SEC | 0:57| 0:50| 0:42| 0:36|
| Tc90/min  | SEC | 8:27| 6:34| 5:15| 4:32|

The phenomenon of frosting is not slight

#### 3.2.2 Peroxide Sulfide System

Peroxide vulcanization is required for special products requiring high temperature resistance (above) and very low compression permanent deformation. The types of peroxides used for EPDM vulcanization at 150°C are as follows: dicumyl peroxide (DCP), 1, 1,2 tertiary butyl peroxide base - 3, 3, 5 - three methyl cyclohexane (Trigonox 29), methyl tertiary butyl peroxide isopropyl benzene (Peikadox14), 2, 5 - dimethyl - 2, 5 - two (tert butyl peroxide) hexane (2, 5), tertiary butyl peroxide isopropyl benzene, etc.

Several commonly used peroxide vulcanizing agents, 2,5, DCP, tx29-40 and TAIC, were selected to vulcanize EPDM. The peroxide vulcanizing masterbatch was tested and the vulcanization characteristics at 170°C were analyzed, as shown in figure 1.

![Figure 1. EPDM peroxide vulcanization curve](image)

The selection of peroxide generally requires comprehensive consideration of vulcanization speed, crosslinking density, storage stability, decomposition temperature, the effect of decomposition products on human body, processing safety and physical and mechanical properties of vulcanizates.
Table 3. Influence of different curing agents on properties of EPDM vulcanizates

| Performance                              | Sulfur vulcanization | Double - 2, 5 | Tx29-40 | DCP | DCP/TAIC |
|------------------------------------------|----------------------|--------------|---------|-----|----------|
| Tensile strength /MPa                    | 12.5                 | 11.1         | 9.9     | 11.6| 11.8     |
| Elongation at break /%                   | 324                  | 223          | 164     | 373 | 256      |
| 100% constant tensile stress /MPa        | 1.83                 | 2.41         | 2.31    | 1.22| 1.83     |
| 300% constant tensile stress /MPa        | 5.65                 | -----        | -----   | 7.22| -----    |
| Vulcanization temperature coefficient K  | 1.68                 | 1.45         | 2.17    | 1.79| 2.14     |
| Reaction activation energy E/kJ. Mol⁻¹   | 83.1                 | 59.22        | 124.18  | 92.77| 121.32   |

Vulcanization temperature coefficient K means to reaches the same degree of vulcanization, the temperature change, the vulcanization time increase or reduces K times. 10°C Therefore, tx29-40 and DCP/TAIC are sensitive to temperature while sulfur and di-2, 5 are less sensitive to temperature.

The reaction activation energy E > 0, the temperature increases, the rate constant increases, the greater the E temperature on the vulcanization rate is more significant. The decomposition rate of peroxide sulfurizer is related to the decomposition activation energy, so the peroxide with appropriate activity should be selected first in the sulfurization process. In order to prevent the molecular chain breaking in the crosslinking process, increase the curing rate, and improve the physical and mechanical properties of vulcanizates, sulfur or sulfur donor or ethylene dimethacrylate (EDMA) and other co-crosslinking agents are usually added to the peroxide crosslinking system.

The chemical name of vulcanization aid TAIC is triallyl isocyanurate, which is a crosslinking agent, a trifunctional monomer, and can be used as a rubber and plastic crosslinking agent. For EPDM, when the peroxide DCP is used as a vulcanizing agent, TAIC is a good vulcanizing aid. When the dosage of TAIC was 0, 1, 2, 3, respectively, the effect of the dosage of TAIC on the vulcanization characteristics of EPDM was studied, as shown in table 4.

Table 4. Influence of TAIC on vulcanization process and physical properties of EPDM

| Dosage of TAIC | 0   | 1   | 2   | 3   |
|----------------|-----|-----|-----|-----|
| Ts1 / min, SEC | 0.58| 0.58| 1.00| 1.01|
| Tc90 / min, SEC| 6.53| 7.12| 7.24| 7.46|
| ML/kg, cm      | 0.59| 0.61| 0.69| 0.71|
| MH/kg, cm      | 8.28| 8.75| 9.19| 9.76|
| Tensile strength /MPa | 12.7| 13.4| 13.2| 12.6|
| Elongation at break /% | 624 | 556 | 536 | 508 |
| 300% constant tensile stress /MPa | 3.90| 4.54| 4.70| 5.03|
| Hardness/shao A | 65  | 66  | 67  | 68  |

The table 4 shows that in the case of DCP dosage must, with the increase of the dosage of crosslinking agent TAIC, the tensile strength of the vulcanizates increased after the first decreases, and tensile elongation decreased, and the crosslink density is gradually enlarged, the crosslinking agent TAIC in the process of sulfide, allyl double bond was open, by unit or the form of a homopolymer with EPDM grafting and crosslinking, surfactant bridge bond formation, improve the system of the crosslinking density, 100% of the vulcanizates, 300% the reach stress increased, while the tensile elongation decreased.

4. Conclusion
(1) The vulcanization rate and the maximum torque of ethyl-propylene rubber were significantly increased by the promoters BZ and lseg-4. Vulcanization speed is fast and not easy to spray frost;
(2) Peroxide tx29-40 can be used to vulcanize EPDM. The activation energy and vulcanization speed are higher than DCP/TAI and DSP 2, 5, which can be used in the high temperature and rapid vulcanization system of peroxide in EPDM.
(3) Adding crosslinking agent TAIC EPDM rubber, rubber vulcanization characteristics and physical properties are improved, and with the increase of dosage, rubber vulcanization rate have obvious increase, and no bloom phenomenon, the maximum torque of vulcanized rubber, tensile strength, 100% and 300% constant tensile stress, shao A hardness as well as the crosslinking density increase.

5. Reference

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