Using KH590-Polybutadiene as the New Compatilizer to Improve Carbon Black / Ethylene-Propylene-Diene Terpolymer Composites

Weili Wu* and Bowen Yu
College of Materials Science and Engineering, Qiqihar University, Qiqihar, 161006, China
wuweili2001@163.com

Abstract. Rubber materials could be widely used with the reinforcement of inorganic materials, the combination of inorganic materials and rubber needs compatilizer that play an important role in the polymeric composites. The ethylene-propylene-diene terpolymer (EPDM) has considerable radiation stability for gamma or neutron radiation, so it can be applied to cable insulating materials. The EPDM has to be reinforced with carbon black (CB) of inorganic fillers, which are hardly compatible with the EPDM matrix due to EPDM saturated bonds. In this work, KH590-polybutadiene (KHBR) was used as a compatilizer to improve interaction between EPDM and carbon black.

1. Introduction
Rubber materials could be widely applied with the reinforcement of inorganic materials or inorganic fillers [1]. EPDM is a polymeric material, of which is usually filled with many kinds of organic or inorganic materials to improve the comprehensive performance for various application purposes [2,3]. EPDM has considerable radiation stability for gamma or neutron radiation, so it can be applied to cable insulating materials [4,5]. However, EPDM has to be reinforced with carbon black (CB) of inorganic fillers, which are hardly compatible with the EPDM matrix due to EPDM saturated bonds [6]. Therefore, the use of coupling agents is inevitable for the blend of inorganic fillers and EPDM [7,8].

The CB is easily to adsorb polybutadiene because of its unsaturated bonds [9,10]. As a result, in this work, KH590-polybutadiene (KHBR) was used as a compatilizer to improve interaction between EPDM and carbon black.

2. Experimental
2.1. Materials
EPDM as grade 23080P and polybutadiene (BR) as grade BR-9000 were produced by Chinese Jilin chemical industrial inc.. Dicumyl peroxide (DCP) as chemical pure was supplied by Shanghai...
chemical reagents company of Chinese medicine group. The other ingredients, such as stearic acid (CA), 2-mercaptobenzothiazole (accelerator M), grease, sulfur (S), (3-Mercaptopropyl) trimethoxysilane (KH590), carbon black (CB) and so on, are all common commercially avail materials obtained in the market.

2.2. Sample preparation
First, the BR was masticated on SK-160 two-roll mill (electrical machinery factory of Tianjin) at 45 ℃ and the nip gap about 1.0 mm for 10 min, and hydrolysis KH590 was added into the BR, in which the mass ratio of KH590 and BR is 1:10, then mixed with the S and half of the CB to product HK590-modified BR (KHBR).

Second, the KHBR was mixed into EPDM matrix, and the mixed rubber was prepared by adding various ingredients, the order of process was EPDM (raw rubbers masticated) → ZnO, CA, accelerator M, KHBR (1, 2.5 and 5 weight percent of EPDM content) → half of the CB → DCP, the preparation process of sample was showed in the Figure 1.

![Figure 1. Reacting mechanism of CB / EPDM composites modified by KHBR.](image)

The formulation of the mixed-EPDM rubber was given in Table 1. The compounds were mixed in a laboratory size (SK-160) mixing mill at a friction ratio of 1:1.1, carefully controlled temperature in the range of 50-60 ℃, the nip gap was 2 mm for 20-30 min and uniform cutting operation. Then the mixture with different compositions was molded in an electrically heated hydraulic press (XLB-D350 × 350) at 180 ℃ for 20 (or t₀ +15) min under 10MPa (optimum curing condition).

| EPDM | CB  | ZnO | Grease | CA   | Accelerant M | DCP | S  | KHBR |
|------|-----|-----|--------|------|--------------|-----|----|------|
| 100  | 40  | 5   | 3.5    | 1.5  | 2            | 2   | 2  | Variable |

2.3. Characterization
Tensile tests were performed on dumbbell-shape specimens according to ISO 37-1994. Shore A hardness was measured on the thickness of 6 mm according to ISO 48-1994 and the tear test was completed according to ISO 34-1994.

The samples were tested and the average of the values was taken. Seven samples were used for each measurement and an average of five readings was taken as the resultant value and removed the maximum and minimum values.

DSC thermal analysis was carried out with differential scanning calorimetry tester (Malvern 204F1, UK), nitrogen purging, and gas flow is set as 50 mL min⁻¹, the temperature ranged from -90 ℃ to -20 ℃ for the samples at a heat rate of 10 ℃ min⁻¹.
Dynamic thermal mechanical analysis (DMA) was performed using a DMA Q800 dynamic mechanical analyzer (TA instrument Co., USA) at a frequency of 1Hz in the temperature range from -100 °C to 0 °C with a heat rate of 5 °C min⁻¹. The storage modulus and tan δ parameters were obtained from DMA analysis. In addition, the thermal stability was analyzed from 15 °C and 550 °C with a TGA/STDA851 thermogravimetric analyzer (Mettler-Toledo Co., Swiss).

The rheological cure properties were determined with MZ 4010 B mark Moving Die Rheometer (MDR, Jiangsu Mingzhu Testing Machinery Co., Ltd. China).

3. Results and Discussion

3.1. Mechanical properties of KHBR-modified EPDM composites

The effects of KHBR content on the mechanical properties of EPDM composites are given as shown in Table 2. Tensile strength was increased with adding KHBR. It is also seen that elastic modulus and Shore A were improved with adding KHBR, the elongation at break decreased a little. The reasons can be interpreted that the addition of KHBR increased the compatibility between EPDM rubber and inorganic filler, resulting in the tensile strength, elastic modulus and Shore A hardness increased. However, when the addition of KHPB was above 5%, the combination of EPDM and CB was firm, increasing the rigidity of materials, so the elongation was falling.

| KHBR (%) | Tensile strength (MPa) | Elastic modulus(MPa) | Elongation at break (%) | Shore A hardness |
|----------|------------------------|----------------------|-------------------------|-----------------|
| 0        | 4.2                    | 0.91                 | 310                     | 38              |
| 1        | 5.6                    | 1.00                 | 290                     | 46              |
| 2.5      | 5.9                    | 1.10                 | 290                     | 46              |
| 5        | 5.4                    | 1.13                 | 260                     | 45              |

3.2. Rheological cure analysis

Curing kinetic and rheometer results are given in Table 3. M_H-M_L increased with the addition of the KHBR up to 2.5%. When the increase of the KHBR content get to 5%, the t_90 was the highest, and the scorch time (t_s2) was minimum for the 2.5% KHBR content. The curing kinetic parameters are calculated and the results are given in Table 3.

Induction period (t_d) values calculated are given in Table 3. The decrease of the t_fir (time required for crosslinking to become unperturbed first-order reaction) showed that the crosslinking reaction started earlier with adding KHBR, the t_fir was the lowest for the 2.5% KHBR, confirming that the lowest scorch time with 2.5% KHBR, M_H-M_L result with 2.5% KHBR is the best, it suggests that the degree of curing is the best.

| Table 3. Curing kinetic parameters. |
|------------------------------------|
| M_H-M_L (N.m) | 0% KHBR | 1% KHBR | 2.5% KHBR | 5% KHBR |
| t_90 (sec)    | 260     | 260     | 260       | 270     |
| t_s1 (sec)    | 80      | 76      | 65        | 76      |
| t_s2 (sec)    | 120     | 114     | 83        | 121     |
| t_d (sec)     | 79      | 76      | 70        | 81      |
| t_fir (sec)   | 140     | 94      | 73        | 83      |

3.3. TGA of KHBR-modified EPDM composites

As is well known, DTG curve represents the weight loss rate of speed, the peak is the fastest temperature of weightloss and it can distinguish weightloss stage usually. DTG curves showed that the
The rate of weight loss was decreased with the addition of KHBR as shown in Figure 2, and the peak height decreased with the increase of KHBR content. It suggests that high or low KHBR content is bad for the thermal properties of EPDM composites. And the composites with 2.5% KHBR have better thermal stability.

![DTG of KHBR-modified EPDM composites](image1)

**Figure 2.** DTG of KHBR-modified EPDM composites.

3.4. DSC of KHBR-modified EPDM composites

DSC thermograms showed that the Tg of 0% KHBR was -56 °C and that of 2.5% KHBR is -61 °C as shown in Figure 3. It was clear that the addition of KHBR decreased the glass transition temperature. It could be considered that the decrease of glass transition temperature (Tg) was most probably due to addition of polybutadiene-based KHBR, which had a much lower Tg than EPDM.

![DSC thermograms of 0% HKBR and 2.5% HKBR](image2)

**Figure 3.** DSC thermograms of 0% HKBR and 2.5% HKBR.

3.5. DMA of KHBR-modified EPDM composites

The change of storage modulus and tan δ were shown in the Figure 4. The storage modulus was increased from 3300MPa to about 8300MPa with adding KHBR. The Tg, taken as the peak temperature of the tan δ curve, was only peak with 2.5% KHBR. However, the peak temperatures
were not the case for 0% and 5% KHBR that was probably due to the inefficient network formation between KHBR and EPDM.

![Storage modulus and temperature graph](image1)

![Tanδ and temperature graph](image2)

**Figure 4.** DMA test results (a) storage modulus and (b) tan δ.

**4. Conclusions**

EPDM composites modified with KH590-polybutadiene were studied in details, in which EPDM was used as a matrix, KHBR used as a compatibilizer. KH590 silane coupling plays an important key role in the rubber formula, the aim is to crosslink inorganic component. The addition of KHBR changed the mechanical and thermal properties of the EPDM. The mechanical properties improved with adding KHBR. EPDM rubber with adding 2.5% KHBR had the better mechanical properties. The results obtained from the MDR, DSC and kinetic studies were consistent and parallel.

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References

[1] Weili W, He H and Zhe C 2019 Sci. Eng. Compos. Mater. 58 209
[2] Seyed M, Ghasem N and Aghil B 2018 Polym. Composite. 39 4071
[3] Amin A, Kandil H, Rabia M, Nashar E and Ismail N 2018 Polym-Plast. Technol. 57 1733
[4] Weili W and He H 2019 J. Polym. Sci. Pol. Phys. 58 330
[5] Dhruba J, Kinsuk N and Nikhil K 2013 Eur. Polym. J. 49 4098
[6] Nicolas C, Oguzhan O, Edith PD, Bouvard L, Pradille C and Billon N 2019 Polymer. 175 329
[7] Benneghmouche Z and Benachour D 2019 Compos. Interface. 26 711
[8] Kato A, Ikeda Y and Kohjiya S 2018 Polym-Plast. Technol. 57 1418
[9] Karaagaç, Bagdagül, Kaner, Damla and Deniz 2010 Polym. Composite. 31 1869
[10] Raut P, Swanson N, Kulkarni A, Pugh C and Janasanhan C 2018 Polymer. 148 247