Natural Rubber Vulcanizate Reinforced by Modified Coal-Shale-Based Fillers

Ming Zhao,[1,2] Yu Xiang[2]

[1]*Department of Chemistry and Environmental Engineering, Chinese Mining University, Beijing 10083, People's Republic of China*
[2]*Department of Mining, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China*

ABSTRACT: Coal shale is considered a waste material in coal mining and washing processes. It comprises both inorganic and organic components. In this study, two kinds of coal shale were microcracked, burned, modified by enoxidation natural rubber (ENR), and then used as reinforcing fillers for natural rubber (NR). The NR vulcanizates reinforced with this modified filler were characterized by bounded rubber content, apparent crosslink density, and various mechanical property tests. The results show that the ultramicro coal-shale powder was a good filler for NR. It could be mixed quickly, and it dispersed well in NR, which resulted in a significant enhancement. After modification by ENR, the reinforcement properties were improved further. The results suggest that this new type of filler could be used as a semireinforcing filler to replace or partially replace carbon black. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1397–1400, 2004

Key words: waste; modification; rubber; fillers

INTRODUCTION

There is a significant amount of coal shale generated in the processes of coal mining and washing, which accounts for about 20% of the final product. It has been treated as an environmentally hazardous byproduct. Currently, most of the refuse is used as filler material for coal mines or as material for road construction. However, some coal shale has the potential to be used as polymer filler.[1] Because coal shale is a mixture of inorganic and organic components, it shows different properties when used as a rubber filler than carbon black or white carbon black. It was the objective of this study to examine the reinforcing mechanism of coal shale as a rubber filler and its effect on other useful properties. We prepared two fillers (samples 1 and 2) based on selected coal from a mine in the Shanxi province of China. The fillers were modified by enoxidation natural rubber (ENR). The mixing experiments were carried out, and the resulting reinforced natural rubber (NR) vulcanizates were studied.

EXPERIMENTAL

Materials

Coal-shale-powder fillers 1 and 2 were made in our laboratory. The main components are shown in Table I. Other materials were commercially available and were used as purchased. The NR was #3 bacon rubber made in China. The ENR was concentrated latex made in China.

Compounding and experimental steps

After purification to remove the impurities, the coal shale was immersed in water for 6–8 h and then in carline at 400–600°C for 1 h. By pulverizing the particles to a controlled size of below 320 mesh (−320 mesh), we obtained powder A. The particle size was measured with a laser grain-size analyzer. By adding ENR into powder A with proper agitation, keeping the solution at ambient temperature for 4 h, and drying at 85°C, we obtained powder B.

The basic recipe included 100 g NR, 5.0 g ZnO, 2.0 g octadecanoic acid, 2.5 g accelerant, 2.5 g sulfur, 1.0 g protective agent, and 0–50 g coal-shale powder (change portions).

Property tests

The mixing test was conducted on an open mixing roll, and the sample was vulcanized in GK-100 (Zhanjiang, China). The tests of vulcanization, extended pulled strength, extended tear percentage, and rack strength were performed by standard methods in conformity to Chinese standards (GB/T9869-88, B/T7042-86, B/T528-1998, GB/T529-91, and GB/T531-92). The bound rubber test was conducted by the following

Correspondence to: M. Zhao (zhaoming57@263.net).

	Component analysis				
No.	W (SiO$_2$)	W (Al$_2$O$_3$)	W (Fe$_2$O$_3$)	W (CaO)	W (MgO)
1	60.50	21.93	4.82	2.02	3.36
2	70.30	13.83	5.74	3.18	3.42

W = weight (%).

method: 0.5 g of gross rubber was placed in a -200 sieve and then immersed in a mixed solvent of gasoline and acetic ether for about 72 h. The insoluble gel was recovered, dried, and weighed:[2]

Rubber content (%)

$$= (\text{Gel weight}/\text{Gross rubber weight}) \times 100\% \quad (1)$$

The apparent crosslink density was defined by $1/Q$, where Q is the swelling:

$$Q = (m - m_0)/m_0 \quad (2)$$

where m_0 is the weight of the rubber sample before swelling and m is the weight of the swelled rubber sample.[3]

The properties of the reinforced coal-shale powder was determined by the equation of Lorenz and De:[4]

$$Q_f/Q_g = ae^{-2} + b \quad (3)$$

where Q_f is the equilibrium swelling with filler and Q_g is the equilibrium swelling with no filler for each gram of the vulcanized rubber absorbed solvent mass (g). The coefficients a and b are special property coefficients; when they are larger, they indicate better reinforcement. z is the filler component in the rubber.

RESULTS AND DISCUSSION

Effects of the gross rubber on the bound rubber quality percentage

The bound rubber quality percentage of the gross rubber is shown in Figure 1. For filler 1B, the bound rubber percentage increased with increasing ENR. The effect was especially obvious in the low-content region. The change in the bound rubber percentage was most drastic when the ENR content was below 7.5%. When the ENR content was over 10%, the bound rubber percentage was almost unchanged. Powder 2B showed a similar trend; when the ENR content was less than 5%, the bound rubber percentage changed dramatically with increasing ENR but then leveled off when the ENR content was above 7.5%. As shown in

Figure 1, at high ENR contents, from 7.5 to 17.5%, powder 1B had a stronger effect on the bound rubber than powder 2B.

When the ENR content was above 7.5%, the powder 2B bound rubber content was considered unchanged. Although the bound rubber of powder 1 increased, the change was insignificant.

It appeared that 7.5% was a very important figure. Figure 1 shows that there was a powerful interaction between filler 2 and ENR, possibly because filler 2 contained many arene components. The arene components could have formed multipolymers with the Si–Al components of filler 2 and contained some active organic groups that could be absorbed physically and chemically by the polar groups of the ENR. The adsorbing reactions could have lowered the flexibility of the ENR molecular chains, increased the rigidity, and lowered the compatibility with NR. As a result, their interactions decreased during mixing.

The results show that there was some bound rubber in the mixture of rubber and the modified coal-shale powder. There was an interface level between the modified powder and NR that could have greatly affected the structures and properties of the NR vulcanizates.[5]

Effects of apparent crosslink density

Figure 2 shows the effect of the apparent crosslink density $(1/Q)$ of the NR vulcanizates. The apparent crosslinking of the NR vulcanizates filled with powder 1B increased with the ENR percentage until the ENR percentage exceeded 15%. There was also a similar trend for the NR vulcanizates filled with powder 2B. However, the latter's heap point was about 9%. Figure 2 shows that if a proper quantity of ENR was added, the compatibility of the interface between the powder and NR improved, resulting in improvement not only on the wet structure of the vulcanizates but also on their antiswollen structure. The interaction became weak between the powder and the rubber, and the
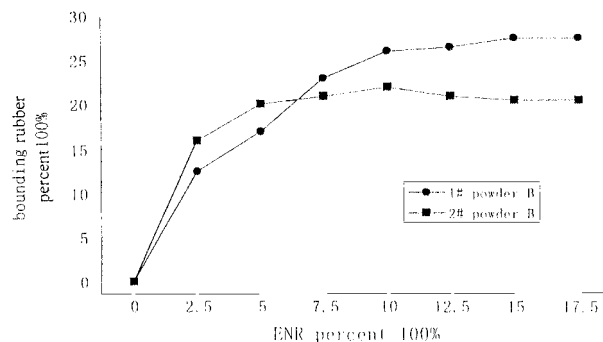

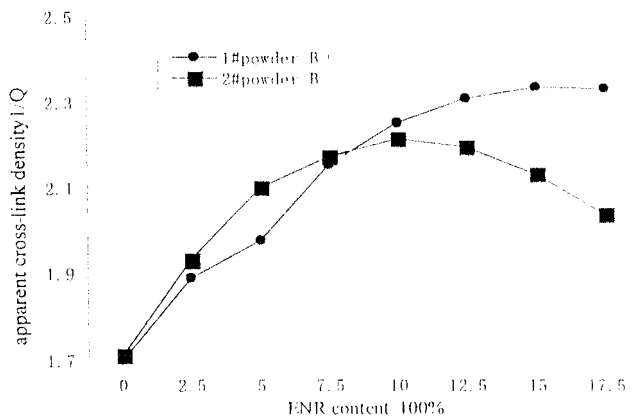**Figure 1** Effect of the ENR content on the bound rubber in the powders.

Figure 2 Effect of ENR content on the apparent crosslink density in the powders.

strength decreased. Additionally, under solvent action, the interface swollen degree increased. The result was that the apparent crosslink density of the NR vulcanizate quality decreased. However, the effect of filler 1 on the NR vulcanizate apparent crosslink density was stronger than that of filler 2. The reason may have been that the NR vulcanizate with filler 2 was less flexible, and the interaction between powder 2 and NR was weaker than that between powder 1 and NR. Moreover, the dispersion of powder 2B in NR may have been poorer than that of powder 1.

Effects on the properties of the NR vulcanizates

Figure 3 shows the reinforcement properties of the vulcanizate filled with coal-shale powder. In Figure 3, one can see the relationship between the vulcanization Q_f/Q_g and the powders; the values of Q_f/Q_g were as follows: $0.30e^{-z} + 1.02$ for powder 1A, $0.32e^{-z} + 1.06$ for powder 2A, $0.46e^{-z} + 0.92$ for powder 2B, and $0.82e^{-z} + 0.74$ for powder 1B.

As shown in Figure 3, when the powder was modified, its reinforcement effects were better. However, before modification, the reinforcement properties of powder 2 were better than those of powder 1. After modification, the reinforcement effects were reversed.
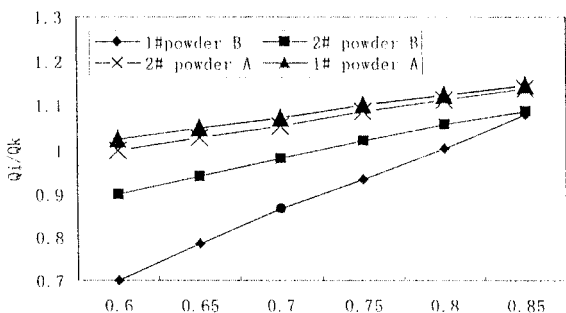

Figure 3 Powder-reinforced curve.

TABLE II
Effects on the Dynamic Mechanical Properties of the NR Vulcanizates Filled with Modified Powder

Property	Quantity of powder 1B				
	0	10	20	30	40
Yong elasticity (%)	74.2	72.3	62.5	57.8	48.2
Yong lag (%)	26.3	26.2	34.8	39.6	49.5
Point modulus		0.41	0.58	0.96	0.96
Effect dynamic Shear modulus (MPa)		3.18	4.92	8.52	10.25
Effect static shear modulus (MPa)	2.54	3.09	4.12	5.83	6.58

Modified powder 1 was better than powder 2. Our explanation is that powder 2 contained more active arene groups than powder 1; these reacted easily with the epoxy groups of ENR. If the ENR content was excessive and the surface layer of the ENR was too thick, the flexibility of the ENR molecular chains would have decreased, and the interaction between the powder filler and NR would have become weaker, so the quality of the modified filler had to be determined by different kinds of coal-shale powder.

Table II shows the effects on the dynamic mechanical properties of the NR vulcanizates filled with modified powder.

As shown in Table II, when the level of filler 1 increased, the rubber elasticity decreased, and the modulus increased. The more interaction there was between the filler and NR vulcanizate, the more segmented was the removed obstruction. In other words, the actual transformation of the filled rubber was bigger that of pure rubber, and the lag effect of filled rubber was also bigger.

Effects on the application properties of NR vulcanizates

Table III shows the main application properties of NR vulcanizates filled with coal-shale powder.

As shown in Table III, ENR was a good modifying agent for the coal-shale powder filler. With the addition of the proper quantity of ENR into the powder, the NR vulcanizate application properties were significantly improved. As we know, there was interaction between ENR and NR, so we believe that ENR formed a link between the filler and NR. This not only increased the coal-shale-powder dispersion in the NR vulcanizate but also improved the NR vulcanizate. Through the link face-level ENR molecule, the web structure effect forced the NR vulcanizate to accept the transfer of the rigid coal-shale powder. The result was that the accepted "street" of the NR vulcanizate matrix decreased and the "interstreet" of the NR vulcanizate was homogenized, which improved the actual NR mechanism properties. In other words, the active

TABLE III
Effects on the Application Properties of NR Vulcanization

Project	Coal shale powder 1	Coal shale powder 2	Modified coal shale powder 1	Modified coal shale powder 2
300% extended stress (MPa)	2.78	2.96	4.35	3.42
Extended strength (MPa)	9.14	10.82	17.13	15.22
Pull strength (kNm)	26.15	26.84	32.52	30.20
Extended tear (%)	576	535	652	608
Tear permanent deformation (%)	42	42	40	40
Shore hardness (°)	45	45	47	47

groups of the coal-shale powder interacted with the epoxy groups of ENR, which decreased the absorption of the vulcanization accelerator and decreased the lag sulfurization. This also improved the value of the coal-shale powder.

CONCLUSIONS

1. Coal-shale powder could be used as a reinforced filler of NR. When it was used as a filler of an NR vulcanizate, ENR could be used as its reinforcing agent. The results show that ENR not only increased the compatibility of the filler and the NR matrix but also improved the web structure of the filled NR vulcanizate.

2. When powder 1 was used, the ENR percentage was about 15%. When powder 2 was used, the percentage was 8–9%. When the ENR percentage was over 7.5%, powder 1 showed better properties than powder 2, but when the ENR percentage was lower than 7.5%, powder 2 showed better properties. When ENR was not used in the powder, coal-shale powder 2 showed better reinforcement effects than powder 1.

3. For the ENR vulcanizate filled with powder 1B, modification increased the 300% extended strength, pull strength, extended tear percentage, and rack strength by 56.74, 87.41, 13.19, and 24.36%, respectively.

4. The higher the use level of the powder was, the higher the polymer segmental motion resistance was. Correspondingly, the filled rubber deformation was larger than that of pure rubber. The lag effects were also larger.

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